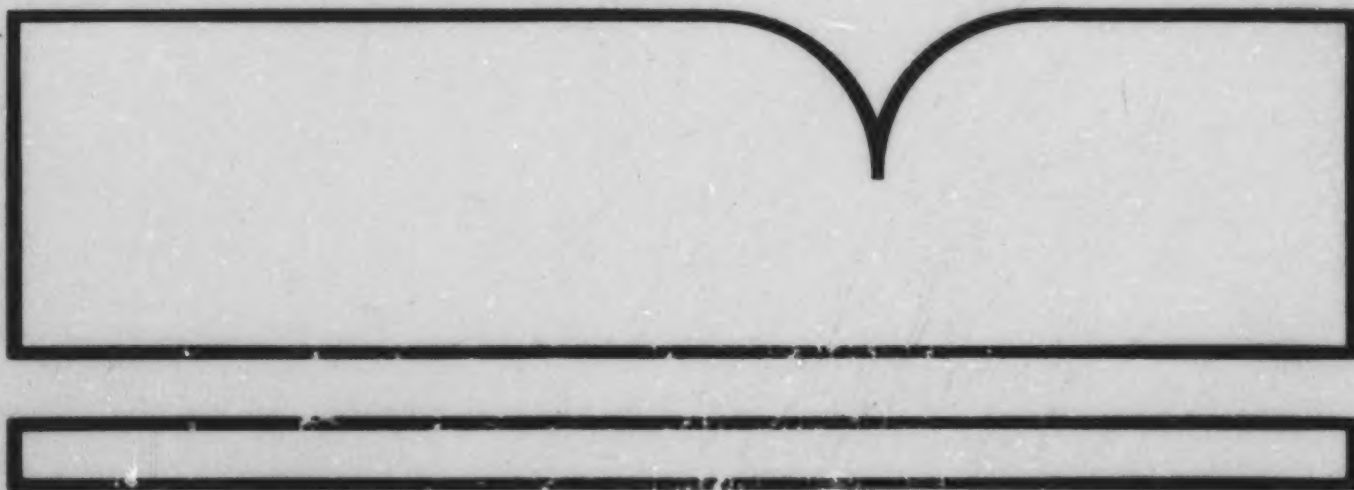


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Incineration and Treatment of Hazardous Waste
Proceedings of the Ninth Annual Research
Symposium Held at Ft. Mitchell, Kentucky on
May 2-4, 1983

(U.S.) Industrial Environmental Research Lab.
Cincinnati, OH

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Sponsored by the U.S. EPA, Office of Research and Development
Municipal Environmental Research Laboratory
Solid and Hazardous Waste Research Division
and
Industrial Environmental Research Laboratory
Energy Pollution Control Division

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related polluttional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

These Proceedings present the results of completed and on-going research concerning the incineration and treatment of hazardous wastes. The information will inform those who own, operate, design, or regulate hazardous waste incineration and treatment facilities of current government-sponsored research in this area. For further information on this subject, interested parties should contact the Incineration Research Branch, Industrial Pollution Control Division, Industrial Environmental Research Laboratory, USEPA, Cincinnati, Ohio 45268.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

These Proceedings are intended to disseminate up-to-date information on extramural research projects concerning land disposal, incineration, and treatment of hazardous waste. These projects are funded by the U.S. Environmental Protection Agency's Office of Research and Development and have been reviewed in accordance with the requirements of EPA's Peer and Administrative Review Control System.

ABSTRACT

The Ninth Annual Research Symposium on land disposal, incineration and treatment of hazardous wastes was held in Ft. Mitchell, Kentucky, on May 2, 3, and 4, 1983. The purposes of the symposium were (1) to provide a forum for state-of-the-art review and discussion of ongoing and recently completed research projects dealing with land disposal, incineration, and treatment of hazardous wastes; (2) to bring together people concerned with hazardous waste management who can benefit from an exchange of ideas and information; (3) to provide an arena for the peer review of the Solid and Hazardous Waste Research Division's and the Energy Pollution Control Division's research programs on hazardous waste management. These Proceedings are a compilation of papers presented by the symposium speakers.

The symposium proceedings are being published as two separate documents. In this document, Incineration and Treatment of Hazardous Waste, seven technical areas are covered. They are as follows:

- (1) Incineration Emissions Measurement Methods
- (2) Lab Scale and Pilot Scale Thermal Decomposition Research
- (3) Evaluation of Emissions from Full-Scale Hazardous Waste Incinerators
- (4) Hazardous Waste Incineration in High Temperature Industrial Processes-Boilers and Kilns
- (5) Methods for Conducting Environmental and Economic Assessment of Hazardous Waste Incinerators
- (6) Innovative Hazardous Waste Control Technology
- (7) Biological Degradation of Hazardous Waste

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DEVELOPMENT OF A VOLATILE ORGANIC
SAMPLING TRAIN (VOST)

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ABSTRACT

The hazardous waste incineration regulations include the requirement that, for selected principal organic hazardous constituents (POHCs), a destruction/removal efficiency (DRE) of $\geq 99.99\%$ must be achieved. In order to calculate meaningful DRE values, reliable sampling and analysis methods must be available. This paper reports on the development and evaluation of a volatile organic sampling train (VOST) for the collection of volatile POHCs from stack gas. The VOST is a method designed by the USEPA as an alternative to the use of integrated gas bulbs and bags. The paper includes data concerning the collection and analysis of four volatile POHCs during the laboratory evaluation, descriptions of the equipment, a description of a field version of the VOST, procedures followed to minimize sample contamination in the field, and conclusions and recommendations from the study.

1.0 INTRODUCTION

The results of previous hazardous waste incineration trial burns have suggested that volatile principal organic hazardous constituents (POHCs) and volatile products of incomplete combustion (PICs) may be important components in the incineration effluents. The sampling technique described in a recent sampling and analysis document (1) for volatile organic compounds involves the collection and analysis of integrated gas bulb and bag samples. However, the authors of that report recognized that the gas bag technique suffers several drawbacks, including the need to position the gas bag in a bulky evacuated sampling box, bag leakage problems, adsorption losses of sample components, contamination problems, and low sensitivity when the bulb or bag is

analyzed using a gastight syringe sampling technique.

To address the need to develop a better sampling and analysis technique for volatile POHCs, personnel from the Environmental Protection Agency (EPA) discussed concepts for a volatile organic sampling train (VOST) with several contracted laboratories. One concept was adopted for development to provide a method to collect a sufficient quantity of volatile POHCs to enable calculation of destruction/removal efficiencies (DREs) as high as 99.999% for incinerators whose waste feed contains as little as 100 ppm of a POHC.

MRI was selected by EPA to carry out a laboratory study to develop and evaluate the sampling train concept. Following the laboratory evaluation of the VOST (2),

a field version of the VOST was designed and built by MRI, and is currently being evaluated under field sampling conditions.

This paper describes how the laboratory evaluation was performed, presents the results of the evaluation, describes the field version of the VOST, and presents conclusions and recommendations based on the results to date.

2.0 VOST CONCEPT

The VOST concept to be evaluated basically consisted of a system designed to draw sample gas at a flow rate of 1 liter/min through two traps in series. The first trap contained Tenax and was preceded by a gas cooler/ condenser and followed by an impinger for condensate collection. A second trap containing a section of Tenax and a section of charcoal was located after the the impinger. The purpose of the second trap was to collect very volatile POHCs (e.g., vinyl chloride), which have low breakthrough volumes and may break through the Tenax trap. In addition, the concept involved replacing both pairs of traps with fresh traps at selected intervals (i.e., every 20 min or 20 liters of sample) over a 2-h sampling period. There were two basic reasons for changing the traps at selected intervals:

- At sample volumes of greater than 20 liters, some of the very volatile POHCs may break through both the front and backup adsorbent traps.
- The changing of the traps allows an initial analysis of one pair of traps. Analysis of a single pair of traps lowers the possibility of collecting too much sample and overloading the GC/MS system. However, if the POHCs are not detected or are present at low levels in the single pair, the option exists of combining the contents of the remaining pairs of traps onto one pair of traps with a concomitant increase in sensitivity. The advantage of the second option for samples with low POHC concentrations is given below.

If a hazardous waste incineration facility is achieving a DRE of 99.999% for a

POHC that is present in the waste at a concentration as low as 100 ppm, the resulting concentration of that POHC in the flue gas will be approximately $0.1 \mu\text{g}/\text{m}^3$ or $0.1 \text{ ng}/\text{liter}$. Sampling 20 liters of that gas will collect only 2 ng of the POHC on a single pair of traps. Since 2 ng may not be detectable by GC/MS analysis, the concept required collection of several (e.g., five) additional pairs of traps and the desorption of their contents onto another pair of traps, thereby providing a total of 10 ng for GC/MS analysis.

It was anticipated that, when the VOST system is used in the field, one will not know whether pairs of traps should be analyzed individually or if the contents of several pairs should be desorbed onto one pair. That is, if the concentration of a selected volatile POHC in the effluent is low (e.g., 0.1 to $1.0 \text{ ng}/\text{liter}$), several pairs may need to be desorbed onto one pair to achieve sufficient analytical sensitivity. However, if the concentration is high, the pair of traps should be analyzed individually, since desorption of the contents of several pairs of traps onto one pair of traps would make the quantity even larger and saturate the GC/MS detector. Therefore, the intent was to use the VOST to collect six pairs of sample traps, but with one pair being analyzed first, individually, to determine the amount of selected POHCs present. Then, if warranted, the contents of some or all of the remaining pairs could be desorbed onto one pair for analysis, or other pairs of traps could be analyzed individually to check the variability in the stack gas composition with time.

The selection of a Tenax front trap and Tenax/charcoal backup trap was based on several factors including the authors' previous experience with adsorbents and information in the literature, primarily from work done at Research Triangle Institute (3). Tenax alone is not a very good adsorber for very volatile organic compounds such as chloromethane and vinyl chloride. Charcoal is a good adsorber for the very volatile organics, but compounds that are less volatile are not easily desorbed from charcoal. Thus the dual trap configuration was considered the most versatile for providing efficient sample collection and recovery of all volatile organics.

The plan was developed to evaluate the VOST concept that consisted of the following:

- Set up an experimental system to generate a wet gas stream prepared with four volatile POHCs at each of four different concentration levels as described in Section 3.1.
- Construct three identical VOSTs that would simultaneously draw gas from the synthetic gas stream.
- Set up equipment for conditioning traps and for thermally desorbing the contents of several pairs of traps onto one pair.
- Set up equipment for analyzing traps by GC/MS.

After the above equipment had been set up and made operational, the plan consisted of carrying out a series of 10 tests. The test runs included: tests at each of four concentration levels, replicate tests at one level, blanks, and a test (also at the replicate level) where the gas contained HCl. The purpose of this last test was to determine if HCl, which is present in many incinerator effluents, had any effect on the analysis results. The order of the tests was randomized to prevent bias from affecting the results. The sequence of the tests in this plan was:

Test	Level (concentration of POHCs in gas)	Comment
1	III (10 ng/l)	Exploratory run to check system
2	0 -	Blank run
3	III (10 ng/l)	
4	I (0.1 ng/l)	
5	II (1.0 ng/l)	
6	IV (100 ng/l)	
7	0 -	Blank run
8	II (1.0 ng/l)	Duplicate of Run 5
9	II-HCl (1.0 ng/l)	Duplicate of Run 5 with HCl in gas
10	0 -	Blank run

The equipment used in carrying out the tests is described in the next section.

3.0 LABORATORY EVALUATION OF THE VOST

This section contains descriptions of the equipment and procedures used in the laboratory evaluation of the VOST including:

3.1 Sample Gas Generator System.

3.2 Sampling Train Design.

3.3 Trap Conditioning Equipment.

3.4 Analytical Procedures.

3.5 Results.

3.6 Summary and Interpretation of Results.

3.1 Gas Generation System

As shown in Figure 1, the gas generation system consisted of 1/2-in. (1.27 cm) stainless steel tubing to carry vaporous N₂ from a liquid N₂ tank through a heater, where the N₂ was heated to about 300°F (149°C). At that point, the N₂ was rendered "wet" by vaporizing deionized/charcoal-filtered water fed through a quartz tube heater. Also near that point, the liquid containing the four POHCs was pumped by a syringe pump (5 ml/h) into the hot N₂ stream where the liquid immediately vaporized to a gas.

The liquid injected by the syringe pump was a solution of the four POHCs, vinyl chloride, carbon tetrachloride, trichloroethylene, and chlorobenzene in methanol.

The concentrations of each of the four POHCs tested are listed in Table 1.

The solution with the highest concentration (Level IV) was prepared first, then aliquots were serially diluted with methanol to prepare the three lower concentration solutions. These same solutions were used as calibration standards for the subsequent analyses.

Following the steam and POHC solution injection point, the gas stream entered a sampling manifold, with a perforated dispersing plate at the inlet. Gases were drawn from this manifold into the three sampling trains. After the manifold, the hot gas (11 to 12 liters/min) passed through a series of impingers (for water

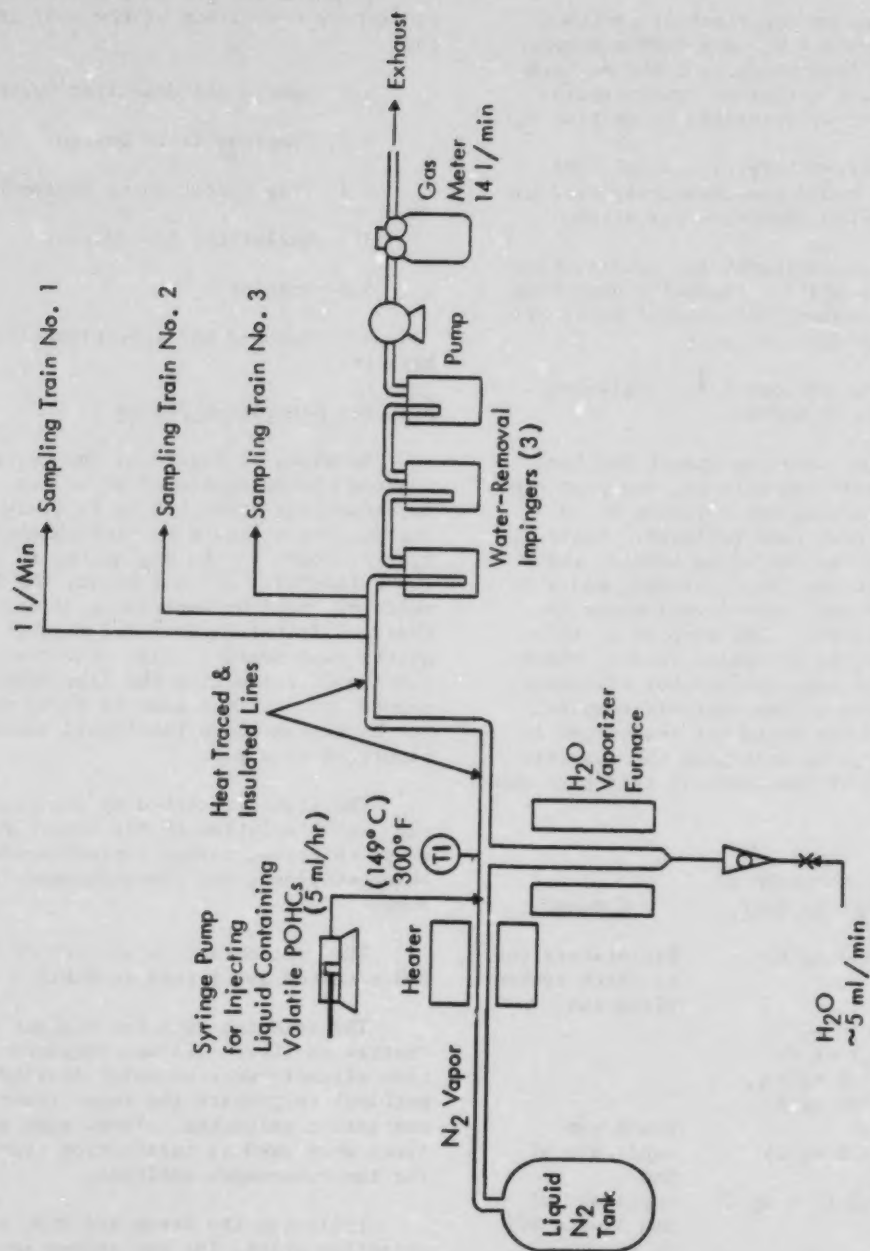


Figure 1. Schematic diagram of laboratory apparatus used to generate and sample a simulated stack gas containing known concentrations of volatile POHCs.

TABLE 1. POHC CONCENTRATIONS TESTED DURING LAB EVALUATION OF THE VOST

Level	Concentration in methanol solution (ng/ml)	Expected conc. in gas stream (ng/l)	Expected amount on each pair of traps (ng)
I	84	0.1	2
II	840	1.0	20
III	8,400	10.0	200
IV	84,000	100.0	2,000

removal) and on through a pump and dry gas meter.

During each of the tests, the gas generation system operated quite well, and all readings were consistent from run to run. The water content of the gas stream ranged from 35 to 37 volume percent, as measured by the impingers and gas meter.

During Run 9, HCl was added to the water at a level of 1.3 g of HCl per liter of water to provide an HCl concentration in the gas of about 0.5 g/Nm³ (normal cubic meter). This is the HCl concentration estimated to occur in the effluent from an incinerator burning a waste containing 15% Cl and equipped with a wet scrubber operating at the relatively low HCl removal efficiency of 95%.

The gas flow rate in the gas generator system and the POHC syringe pump injector rate were used to compute an "expected value" for the quantity of each POHC in the Tenax traps. It was not feasible within the scope and time frame of this project to quantify the actual concentration of the POHCs in the gas produced by the gas generator system. An independent analysis of the spiked gas stream would have been desirable but very difficult to accomplish; however, the subsequent VOST data gave little or no reason to believe that the actual gas stream concentrations were significantly different than the computed "expected values."

3.2 Sampling Train Design

Figure 2 shows the VOST configuration that was evaluated. The train consisted of:

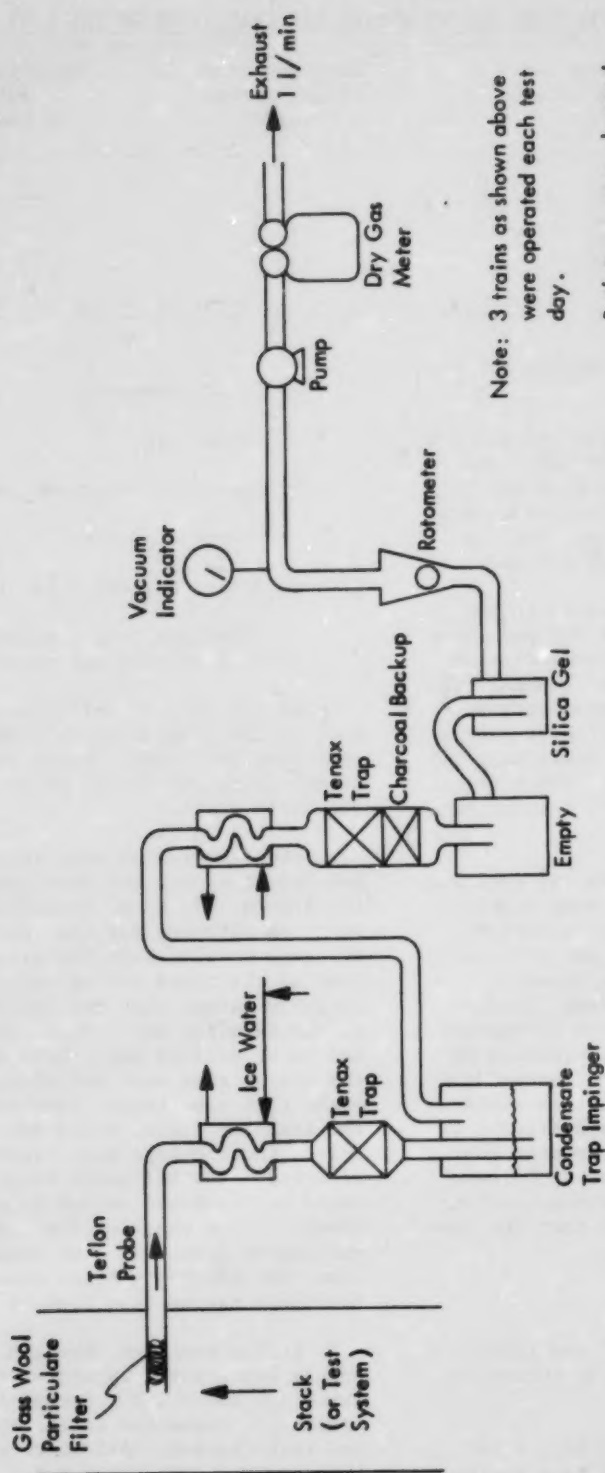
A sampling line (1/4-in., 0.64 cm, Teflon tubing in the test system);

- First condenser;
- Tenax trap;
- Impinger (for condensate removal);
- Second condenser;
- Tenax/charcoal trap; and
- Other sampling components (rotometer, pump, dry gas meter).

Except for the Teflon sampling line, most of the components were made of glass, including the traps. However, the fittings at the inlet and outlet of each trap were stainless steel.

When the trains were initially assembled, two problems developed. First, the 5/8-in. (1.58 cm) stainless steel Swagelok fittings for the inlet traps were designed to slip over the glass trap, but some of the traps had an outside diameter slightly larger than the inside diameter of the Swagelok nut. Thus, all the nuts had to be drilled out. Secondly, some of the glass traps were out-of-round. This meant that some traps, when inserted into the sampling train, would not leak-check unless the fittings were tightened with wrenches. Several tubes broke before they could be tightened enough to pass a leak-check. Since checking for leaks and correcting of leaks can take considerable time, the adsorbent traps were redesigned for field use as described in Section 4.0.

Before each run, the gas generation system was started up and allowed to operate for about 1 h. During that time, traps were connected in the three trains and leak-checked. All three trains were then started and operated for 20 min at



Note: 3 trains as shown above were operated each test day.

Both traps were changed every 20 minutes over 2 hour period.

Note: Tenax & Tenax/charcoal traps were 1.6 cm in diameter & 10 cm long

Figure 2. Volatile organic sampling train (VOST).

about the same rate (1 liter/min).^{*} All three sampling trains were then shut off and the traps removed and placed in pre-marked container tubes. Another pair of traps were then inserted in each train and leak-checked before starting the next 20-min sampling period. A run was considered complete after six pairs of traps had been used in each train. During each run, ice water was circulated through the condensers. Thermocouples, located against the surface of the condenser outlet tubes, indicated that the gas temperature entering the first trap was in the range of 60 to 80°F (16 to 27°C). (The train with the longest Teflon sampling tube yielded the lowest temperature.)

Overall, the train configuration caused no particular difficulty, except for the leak-check problem described above. However, using this train configuration to sample a "wet" gas stream saturates the first trap with condensate. This caused no problems in the sampling but did require development of special procedures for analyzing the wet traps, as discussed in Section 3.4.

3.3 Trap Conditioning Equipment

The trap conditioning/desorption apparatus, purchased from Nutech^{**} (Model No. 322), served two purposes for the VOST evaluation. First, it was used to condition traps prior to use, by heating them at 250°C for 4 h with an estimated flow of 30 ml/min of purified nitrogen gas through each trap. Second, it was used to thermally desorb the contents from each of several low-level pairs of traps onto one pair of traps for GC/MS analysis. The purpose of this desorption/adsorption was, in effect, to further concentrate the samples from the sampling train.

A schematic diagram of the conditioning/desorption apparatus is shown in Figure 3, along with the trapping system that was added at the outlet to re-adsorb the contents from the desorbed pairs of traps.

^{*} Gas flow rates in liters per minute refer to normal conditions of 20°C, 1 atm (dry basis).

^{**} Nutech Corporation, 2806 Cheek Road, Durham, NC 27704.

When four traps were being desorbed (which is the capacity of one section of the desorption apparatus), the carrier gas (N₂) exits the desorption chamber hot, but cools rapidly. However, when the traps being desorbed are wet, the cooling is not nearly so rapid because of the steam that must be condensed. Thus, it was necessary to use a condenser at the outlet of the conditioning equipment, in front of the first trap (Tenax). An impinger was also required to remove the condensate before the desorbed gas passed into the second trap. As a result, the re-adsorption system of traps at the outlet of the desorption equipment is equivalent to the sampling train itself. Also, the condensed steam again wets the first trap, so the need to analyze a wet trap still remains.

When using the Nutech conditioning apparatus to desorb several pairs of traps (e.g., five pairs), the conditioner was first heated to its normal operating temperature of 250°C. Four traps were then dropped into the chambers and allowed to remain there for 10 min (with the total N₂ carrier flow of 120 ml/min passing through the four traps). These four traps were then removed and four more traps inserted, repeating the procedure until all five pairs had been desorbed onto the one pair at the outlet. This pair, or any pair analyzed individually without first being desorbed, was then spiked with an internal standard and analyzed using the equipment and procedures described in Section 3.4.

3.4 Analytical Procedures

The analytical procedures described below include cleanup of the Tenax and charcoal prior to packing into traps, preparation of the traps, conditioning of the traps prior to sampling, spiking of the traps with an internal standard following sampling, GC/MS analysis of the traps, and data reduction.

3.4.1 Tenax and Charcoal Cleanup--

The Tenax (35/60 mesh) and SKC petroleum-based charcoal (Lot No. 104) were initially prepared by Soxhlet extraction for 24 h with methanol and then with pentane. The sorbents were then dried in a vacuum oven at 100°C for 6 h prior to loading into empty traps, each engraved with a unique number.

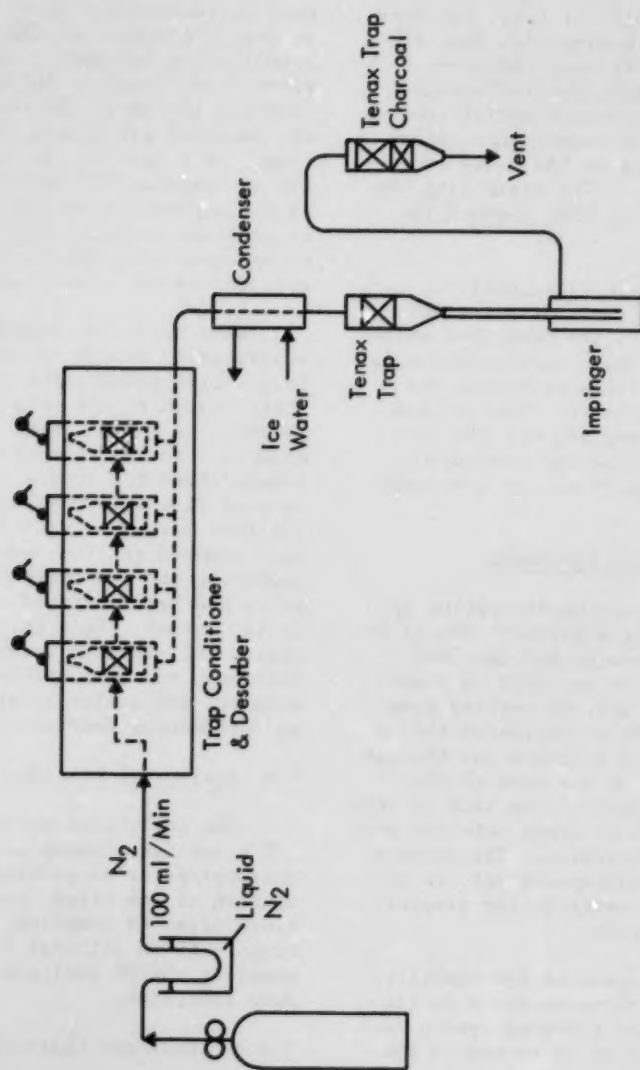


Figure 3. Schematic diagram of trap conditioner/desorption apparatus.

3.4.2 Preparation of Traps--

The 10- x 1.6 cm glass traps with one nipped end (to facilitate removal of the traps from the desorption apparatus with tweezers), available from the Nutech Corporation, were used for the VOST evaluation. A minimum amount of pre-extracted and oven-dried glass wool was used in each of the glass tubes to hold the sorbents in the glass traps. The all-Tenax traps contained about 1.6 g of Tenax, and the Tenax/charcoal traps contained about 1 g of Tenax and 1 g of charcoal (two-thirds Tenax by volume).

3.4.3 Trap Conditioning--

The traps were thermally conditioned prior to use, using the Nutech Model 322 thermal conditioning unit. The conditioning gas (nitrogen or helium) was purified by passing through a U-trap containing a 5-angstrom (5×10^{-8} cm) molecular sieve with the U-trap immersed in liquid nitrogen. The temperature of the conditioning unit was adjusted to 240 to 250°C, and the flow rate of gas through each trap was estimated to be about 30 ml/min. However, only the sum of the flow through four of the traps, which was set at 120 ml/min, could actually be measured with the Nutech conditioning unit. The traps were conditioned for at least 6 h prior to their first use in the VOST evaluation and for at least 2 h more prior to use in sampling. The actual flow through each trap may be lower due to the fact that some of the conditioning gas may flow around rather than through the traps. Also residual pentane was observed during several subsequent analyses of the traps, suggesting that the conditioning step was not completely effective.

Following conditioning, each trap was transferred to a clean 25- x 150-mm screw-cap test tube engraved with the same unique number as engraved on the trap. The traps were then ready for sample collection or spiking experiments.

3.4.4 Spiking of Traps with Internal and Calibration Standards--

Prior to GC/MS analysis, all Tenax and Tenax/charcoal adsorbent trap samples and standards were spiked with 25 ng of perfluorobenzene (PFB) internal standard using the flash vaporization technique in

which the spiking solution is vaporized and carried onto the trap with a carrier gas. The glass traps were attached to the injection port (160°C) of a GC with a 5/8-in. (1.58 cm) stainless steel Swagelok nut containing Teflon ferrules. The Swagelok fitting was connected to the GC column connection via a reducing fitting. The helium flow through the traps was set to about 50 ml/min. The gas flow through the trap was turned on and off using the shutoff valve on the side of the Varian 1400 GC.

The spiking solution was loaded and expelled from the syringe using the solvent flush technique to ensure that the standard solution would be completely expelled from the syringe. To use this technique, the needle of a 5.0 µl syringe was filled with clean methanol. The methanol was then expelled leaving methanol only in the syringe needle. Then air was drawn into the syringe to the 1.0 µl mark followed by a 25-ng/µl methanolic solution of the PFB to the 2.0 µl mark. The gas flow was turned on through the trap and the syringe needle inserted through the GC septum port. The contents of the syringe were then slowly expelled over about a 15-s period. At the end of about 25 s, the gas flow through the trap was shut off and the syringe removed. All POHC calibration standards were spiked using exactly the same procedure. The total flow of gas through the traps during spiking was thus only about 25 ml.

3.4.5 GC/MS Analysis of the Traps--

To analyze the traps, the contents of the wet traps (dry traps in the case of method blanks, field blanks, and calibration standards) were thermally desorbed using a stream of carrier gas into a water column (1 to 5 ml); this is a component of the EPA Method 624 purge-trap-desorb GC/MS analysis system. A schematic diagram of the apparatus is shown in Figure 4. The sample trap was dropped into the desorption chamber and desorbed at a flow rate of 100 ml/min for 10 min at 180°C. The desorbed compounds passed into the bottom of the water column, were purged from the water, and then were collected on an analytical adsorbent trap also containing Tenax and charcoal. The compounds were then desorbed from the analytical adsorbent trap into the GC/MS system per EPA Method 624.

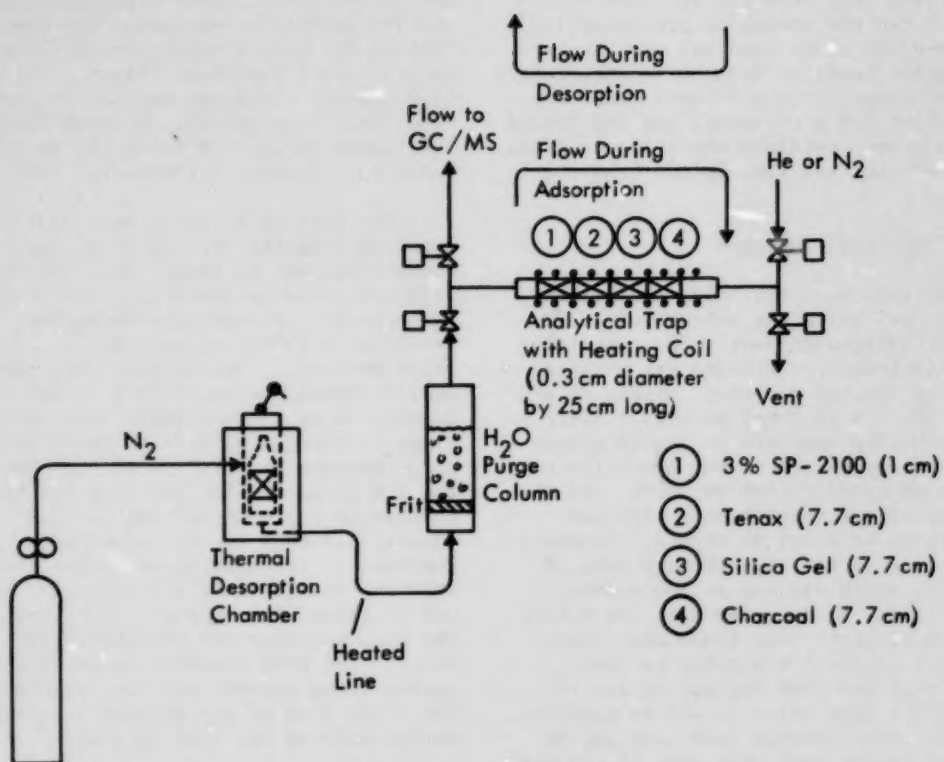


Figure 4. Schematic diagram of trap desorption/analysis system.

The normal routine for analyzing a set of traps from each of the laboratory VOST evaluation runs was to analyze a calibration standard on Tenax, a calibration standard on Tenax/charcoal, and then to intersperse calibration standards about every fourth sample. Blank Tenax and blank Tenax/charcoal traps (conditioned traps spiked with internal standard) were also analyzed when the samples from the blank VOST train were analyzed. The same POHC solution used to spike the wet gas in the VOST runs was used to prepare the calibration standards for quantification of the POHCs on the traps.

The problem of analyzing the wet sample traps was overcome by desorbing the contents of the wet traps into an aqueous purge and trap apparatus. Since the purge and trap technique initially appeared to offer minimal risk of losing or affecting the very small amounts of each compound to be quantified (i.e., 2 to 10 ng of POHC), and was basically consistent with an accepted EPA method, it was used in this evaluation. The Nutech apparatus was initially tested in the normal cryogenic trapping configuration, but the desorbed water froze and clogged the analytical system. Other wet trap analysis techniques were considered but not investigated because of lack of time and possible associated problems.

3.4.6 Data Reduction--

The POHCs in the samples were quantified using the internal standard technique. The area of the masses of m/z 62 for vinyl chloride, m/z 117 for carbon tetrachloride, m/z 130 for trichloroethylene, m/z 112 for chlorobenzene, and m/z 186 for the perfluorobenzene internal standard were used to calculate response factors from analysis of the 8.4- and 84-ng calibration standards according to the equation:

$$\text{Response Factor (RF)} = \frac{(A_S)(C_{IS})}{(A_{IS})(C_S)}$$

where: A_S = The area of ion for the POHC.
 A_{IS} = The area of the ion for the internal standard (m/z 186).
 C_{IS} = The amount of internal standard (25 ng).
 C_S = The amount of POHC in the calibration standard (generally 8.4 or 84 ng).

The amounts of the POHCs in the samples were then calculated according to:

$$\text{Amount of POHC} = \frac{(A_S)(C_{IS})}{(A_{IS})(RF)}$$

The reproducibility of the internal standard area counts (m/z 186) was very good with an average variation of only about 10% for a daily batch of samples at a given multiplier setting. There did not appear to have been any particular difference in perfluorobenzene area counts with the type of trap; e.g., wet traps or Tenax/charcoal traps did not give lower area counts than dry traps and Tenax-only traps. This is in contrast to the POHC vinyl chloride which gave higher response on Tenax than on Tenax/charcoal traps during analysis of calibration standards. The reason for this is as yet undetermined. There is no reason to believe that the vinyl chloride broke through the Tenax to the charcoal because only about 15 ml of gas passes through the trap during spiking.

3.5 Results

It was noted in Section 2.0 that a total of 10 runs were made during this evaluation, involving four different concentration levels of the POHCs and three blank runs. After each run, the traps from each of the three trains were analyzed and results reported for the traps as pairs (i.e., Tenax trap plus Tenax/charcoal trap). Not all pairs were analyzed, especially at the higher concentration levels, where it was not necessary to desorb several pairs onto one pair. In most cases, at the lower concentration levels, one pair of traps from each train were analyzed individually, while all remaining pairs from each train were desorbed onto a single pair for analysis. Several calibration standards were analyzed along with the traps from each run in order to be able to quantify a wide concentration range.

Results were initially calculated after each run based on calibration standards analyzed with the samples from each run. After all runs and analyses had been completed, the results were recalculated based on the average mass spectrometric response factor of all the appropriate calibration runs using the internal standard technique described earlier in Section 3.4.6. These response factor data are

shown in Table 2. The data in Table 2 also show transfer efficiencies determined for desorbing several pairs of traps with re-adsorption onto a single pair. Since the transfer efficiency for vinyl chloride was relatively low (49%), the reported values for vinyl chloride were corrected for this low transfer efficiency. Also, the data for the four POHCs were blank-corrected, as discussed below.

Three blank runs were carried out using the gas generation system and three VOSTs, but without any injection of the solution containing the POHCs into the system. The results for these blank runs are shown in Table 3 and include analyses of single pairs, and several pairs combined onto one pair. As can be seen in Table 2, most of the blank values are relatively low, but are still significant relative to the run at the lowest concentration level where the expected amount of any POHC on each pair was only about 2 ng. In this regard, the blank values for carbon tetrachloride in Runs 7 and 10 are higher than the expected value. Thus, it was not possible to blank-correct the carbon tetrachloride results obtained in the lowest level run (Run 4), which makes it difficult to make any definitive conclusions about using the VOST train for detecting such low levels of carbon tetrachloride.

The problem with the high carbon tetrachloride blanks was evident after Run 7, and therefore another blank run was made (Run 10), after the gas generation system and the trains were purged with vapor from the liquid N_2 tank at room temperature for 24 h. However, the blank carbon tetrachloride values were again found to be high in Run 10. Other blank traps were analyzed which had not been exposed to the gas generation system, but had been exposed to room (laboratory) air, and no POHCs were detected in these blanks (i.e., < 0.5 ng). The absence of carbon tetrachloride in the blanks suggested that the high blank values for carbon tetrachloride resulted from within the gas generation system or the sampling trains and was not a result of any subsequent analytical procedures or contamination from the ambient room air.

Except for the carbon tetrachloride data from the lowest level run, all uncorrected and blank-corrected results were tabulated, with the corrected values being used to compute the results as a percentage

of the expected value. These tabulated data are summarized in Table 4. The data in Table 3 provide information on results computed as averages but do not show the range in results. The compounds are discussed individually below.

3.5.1 Vinyl Chloride--

Figure 5 (for vinyl chloride) shows all results, blank-corrected and corrected for the 49% transfer efficiency when transferring the contents of several pairs of traps onto one pair.

The results for vinyl chloride at the 0.1 and 1.0 ng/liter gas phase concentrations appear to be similar, with total recoveries when analyzing single pairs ranging from 48 to 95% of the expected value. When combined pairs were used the recoveries ranged from 48% of the expected value up to 148%. Conversely, at the 10 ng/liter level where only single pairs were analyzed, all except one data point are greater than the expected value, ranging from 100 to 180% of the expected value. This is a rather wide range, but vinyl chloride is very volatile, and it is commonly recognized that analyses for this compound are difficult.

At the highest concentration level (Level IV, 100 ng/liter gas-phase concentration, 2,000 ng/pair of vinyl chloride expected on the traps), the results were consistently low (~ 48% recovery). Although nearly all of the other POHCs were consistently found on the first Tenax trap of any pair, most of the vinyl chloride was found on the backup Tenax/charcoal trap. The data thus suggest that breakthrough or irreversible adsorption of the vinyl chloride occurred at the highest concentration level. Thus in any further testing, one should be aware that this may occur when using the VOST method at high concentrations of vinyl chloride.

3.5.2 Carbon Tetrachloride--

The results for carbon tetrachloride are shown in Figure 6. These data are all blank-corrected except for the data at the lowest concentration level. As a consequence, the data at the 0.1 ng/liter level exhibit some very high values, which undoubtedly are not representative.

TABLE 2. GC/MS RESPONSE FACTOR AND THERMAL DESORPTION COLLECTION EFFICIENCY FOR FOUR VOLATILE POHCs

Compound	Avg. RF ^a	σ	% RSD ^b	n ^c	Type of trap	RF ^f following desorption	n	Desorption transfer efficiency
Vinyl chloride	0.140	± 0.042	30	15	T/C ^d	0.069	2	49
Carbon tetrachloride	0.197	± 0.069	35	13	T ^e	0.143	2	73
Trichloroethylene	0.490	± 0.068	14	14	T	0.435	2	89
Chlorobenzene	0.338	± 0.065	19	14	T	0.331	2	98

^a Mass spectrometric response factor relative to perfluorobenzene.

^b RSD = Percent relative standard deviation, which equals $\sigma \div \text{Mean} \times 100$.

^c n = Number of determinations (includes 8.4 and 84 ng calibration standards).

^d T/C = Tenax/charcoal (~ 70:30 v/v) trap.

^e T = All-Tenax trap (1.6 g).

^f Contents of calibration standard thermally desorbed onto type of adsorbent trap in previous column.

TABLE 3. TABULATION OF DATA FROM BLANK RUNS

Blank run No.	No. of combined pairs	Amount detected (ng) ^a			
		Vinyl chloride	Carbon tetrachloride	Trichloro- ethylene	Chloro- benzene
<u>Single pairs data</u>					
2		----- No single pairs analyzed -----			
7		< 0.5	12.5	0.7	0.8
7		< 0.5	3.6	0.2	0.6
7		< 0.5	3.5	< 0.5	< 0.5
10		< 0.5	1.2	3.4	< 0.5
10		< 0.5	3.7	< 0.5	< 0.5
10		< 0.5	< 0.5	2.0	< 0.5
Avg for single pairs ^b		0	4.1	1.1	0.2
<u>Combined pairs data</u>					
2	4	5.4	< 0.5	2.3	8.0
2	4	4.8	< 0.5	2.5	6.4
7	5	4.7	35	5.0	8.1
7	5	1.1	49	6.6	10.0
7	5	Lost	17	6.3	4.0
10	5	< 0.5	53	4.8	1.8
10	5	< 0.5	50	2.2	3.6
10	5	< 0.5	54	3.0	6.2
Average per pair for combined pairs		0.5	6.8	0.9	1.3

^a Amounts calculated based on average response factor determined from all standards (response factor for VC was based on analyzing standards on Tenax/charcoal traps; the other compounds were based on analyzing standards on Tenax traps).

^b Less than values were assumed to be zero in order to compute an average.

TABLE 4. VOST DATA SUMMARY

Run No.	Expected gas phase concentration of each compound (ng/liter) ^a	No. of cartridge pairs analyzed (i.e., replicates)	No. of cartridge pairs combined for analysis	Average expected value (ng)	Average amount found, in ng, - blank corrected, and (% of average expected value) ^d					
					Vinyl chloride ^c		Carbon tetrachloride ^d		Trichloroethylene	
					Single pairs	Combined pairs	Single pairs	Combined pairs	Single pairs	Combined pairs
2	0	2	4	0	-	5.1	-	< 0.5	-	-
7	0	3	0	0	< 0.5	-	6.5	-	2.4	7.2
7	0	3	5	0	-	2.9	-	34	0.3	0.5
10	0	3	0	0	< 0.5	-	1.6	-	6.0	7.4
10	0	3	5	0	-	< 0.5	-	52	1.8	< 0.5
4	0.1	2	0	1.9	1.5(79%)	10.1(111%)	4.2(221%) ^d	16(176%) ^d	3.3	3.9
4	0.1	3	5	9.1	-	-	-	-	1.5(79%)	1.8(95%)
5	1.0	3	0	19	12(63%)	-	9(47%)	22(116%)	8.8(97%)	9.5(106%)
5	1.0	3	4	77	-	37(48%)	-	-	-	-
8	1.0	3	0	20	17(85%)	-	11(55%)	68(88%)	83(108%)	29(153%)
8	1.0	3	4	78	-	115(146%)	-	23(115%)	23(115%)	101(131%)
9	1.0 (with HCl)	3	0	20	19(95%)	-	8(40%)	89(113%)	83(105%)	21(105%)
9	1.0 (with HCl)	3	4	77	-	61(79%)	-	19(95%)	19(95%)	91(115%)
3	10.0	7	0	193	274(142%)	-	136(70%)	85(110%)	81(105%)	18(90%)
3	10.0	-	0	-	-	-	-	-	210(109%)	74 (96%)
6	100.0	6	0	2,020	870(43%)	-	2,180(108%)	-	-	204(106%)
6	100.0	-	0	-	-	-	-	-	2,660(132%)	2,050(101%)

^a Gas volume in liters refers to dry standard conditions (20°C, 1 atm).

^b Cartridge pairs refers to one Tenax cartridge and an associated Tenax + charcoal cartridge.

^c Data for vinyl chloride include correction for 49% transfer efficiency when several pairs are desorbed onto one pair (per Table 1).

^d All values are blank-corrected except for carbon tetrachloride in Run 4, due to large average blank value (per Table 2).

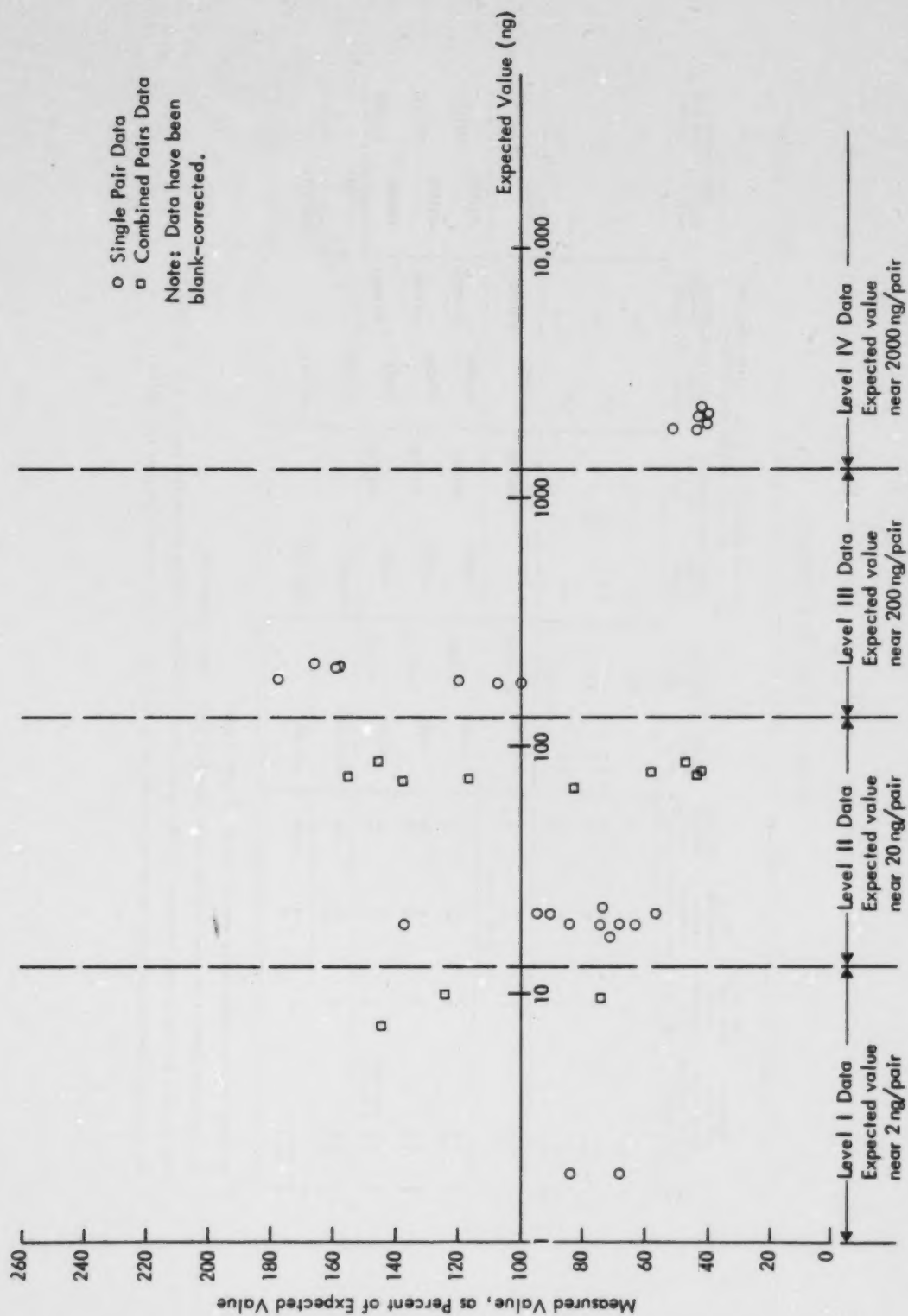


Figure 5. Vinyl chloride test results.

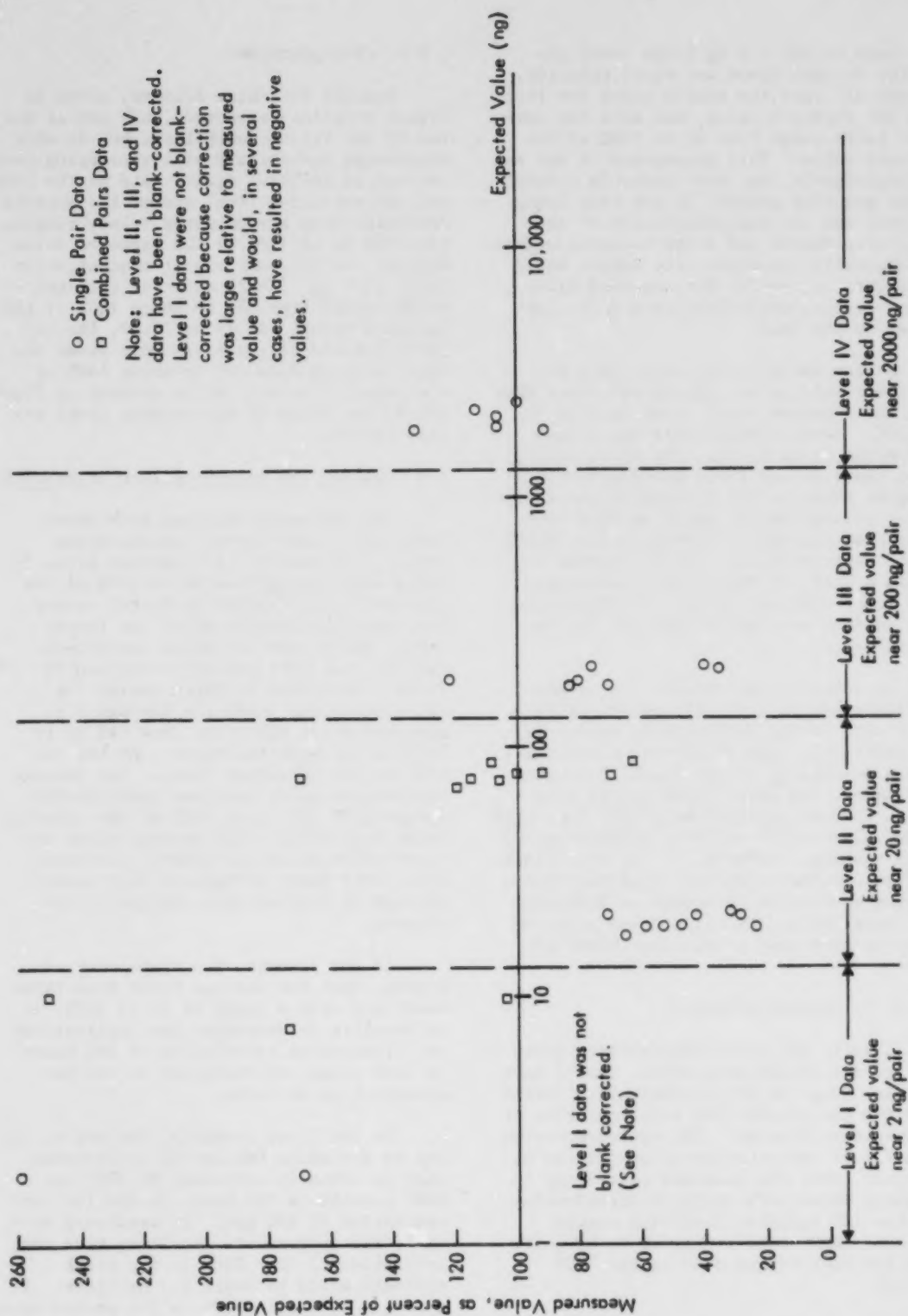


Figure 6. Carbon tetrachloride test results.

Data at the 1.0 ng/liter level are similar to that found for vinyl chloride, in that all data for single pairs are less than the expected value, but data for combined pairs range from 60 to 170% of the expected value. This phenomenon is not as yet explainable, but most probably relates to the quantity present on any trap being analyzed and the characteristics of the purge-trap-desorb and GC/MS analysis method. As originally conceived, the intent would be to rely on results for combined pairs at low levels, which does seem to be supported by the data.

At the 10 ng/liter level, data for all the single pairs, except one, were less than the expected value, ranging from 36 to 120%. Thus, a result for any single pair might be quite low, but it is anticipated that, in any field testing, results would be based on the average of the analysis of several pairs, which in this case would have yielded an average value of 70% of the expected value. It is evident in Figure 6 that, at the highest concentration level (100 ng/liter), all the single pair results were quite close to the expected value.

In summary, the results for carbon tetrachloride do not indicate any major deficiency in the VOST method, except for the relatively high blank values and their effect on results at the lowest concentration level. If these blank values were due to the gas generation system, then high blank values might not be a problem in any field testing. However, if the high blanks somehow resulted from the sampling trains, further work would be needed to determine how trains should be cleaned and prepared prior to each test to minimize blank problems.

3.5.3 Trichloroethylene--

Results for trichloroethylene, given in Figure 7 (blank-corrected), show a much narrower range at all concentration levels than did the results for vinyl chloride or carbon tetrachloride. The extremes varied from 70% of the expected value (at the 0.1 ng/liter level for combined pairs), up to slightly above 140% of the expected value (at the 100 ng/liter level for single pairs). These results appear to be quite good for this compound using the VOST method.

3.5.4 Chlorobenzene--

Results for chlorobenzene, given in Figure 8 (blank-corrected), are not as narrow as for trichloroethylene, but do show decreasing variability with increasing concentration levels. Again, data at the lowest concentration level showed the greatest deviation from the expected value, ranging from 36% up to 173% of the expected value. However, at the next higher concentration level (1.0 ng/liter), data for combined pairs ranged from 88% to about 140% of the expected value. At 10 ng/liter, the results for the single pairs were about the same, ranging from 70% to about 140% of the expected value. As is evident in Figure 8, the range at the highest level was very narrow.

3.6 Summary and Interpretation of Results

The preceding sections have shown that, at the two lowest concentration levels, the results for combined pairs of traps might range from 38 to 173% of the expected value (excluding higher values for carbon tetrachloride at the lowest level, which were not blank-corrected). However, the data presented earlier in Table 4 show that if three trains (or three runs) are used, the average for combined pairs may range from 48% up to 146% of the expected value. At the two highest concentration levels, the average for several pairs analyzed individually ranged from 70% up to 142% of the expected value (excluding a 43% average value for vinyl chloride at the highest concentration level where it appears that breakthrough or irreversible adsorption occurred).

If one assumes, for simplicity of number, that the average value from three tests may span a range of 50 to 150%, it is possible to determine the implications on a subsequent calculation of DRE based on that range, as explained in the two scenarios given below.

In the first scenario, one may be trying to determine DRE for an incinerator that is actually achieving 99.999% for a POHC present in the waste at the low concentration of 100 ppm. As mentioned earlier, the approximate resulting true concentration of that POHC in the stack effluent would be about 0.1 ng/liter. If this gas is sampled over a 2-h period using

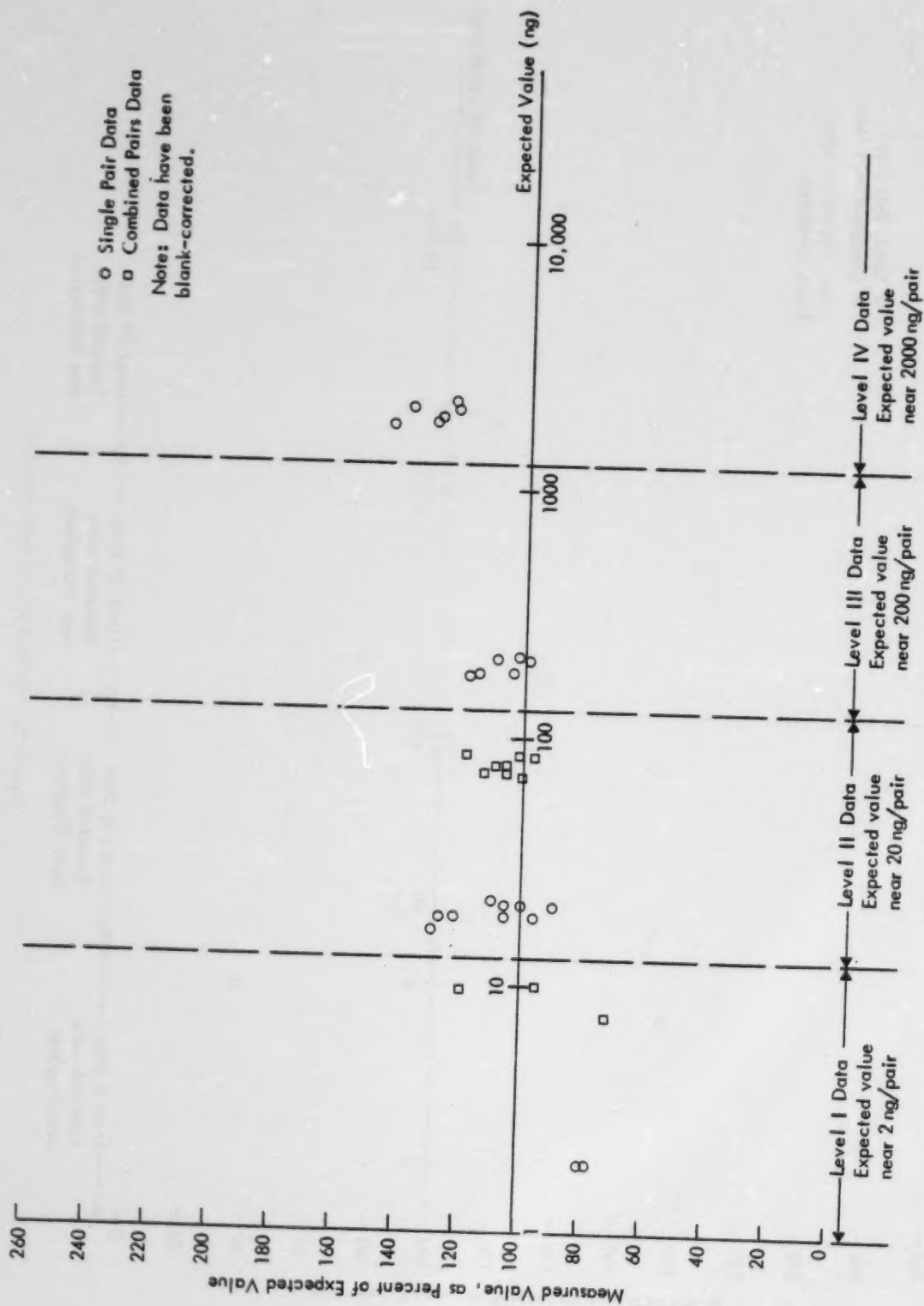


Figure 7. Trichloroethylene test results.

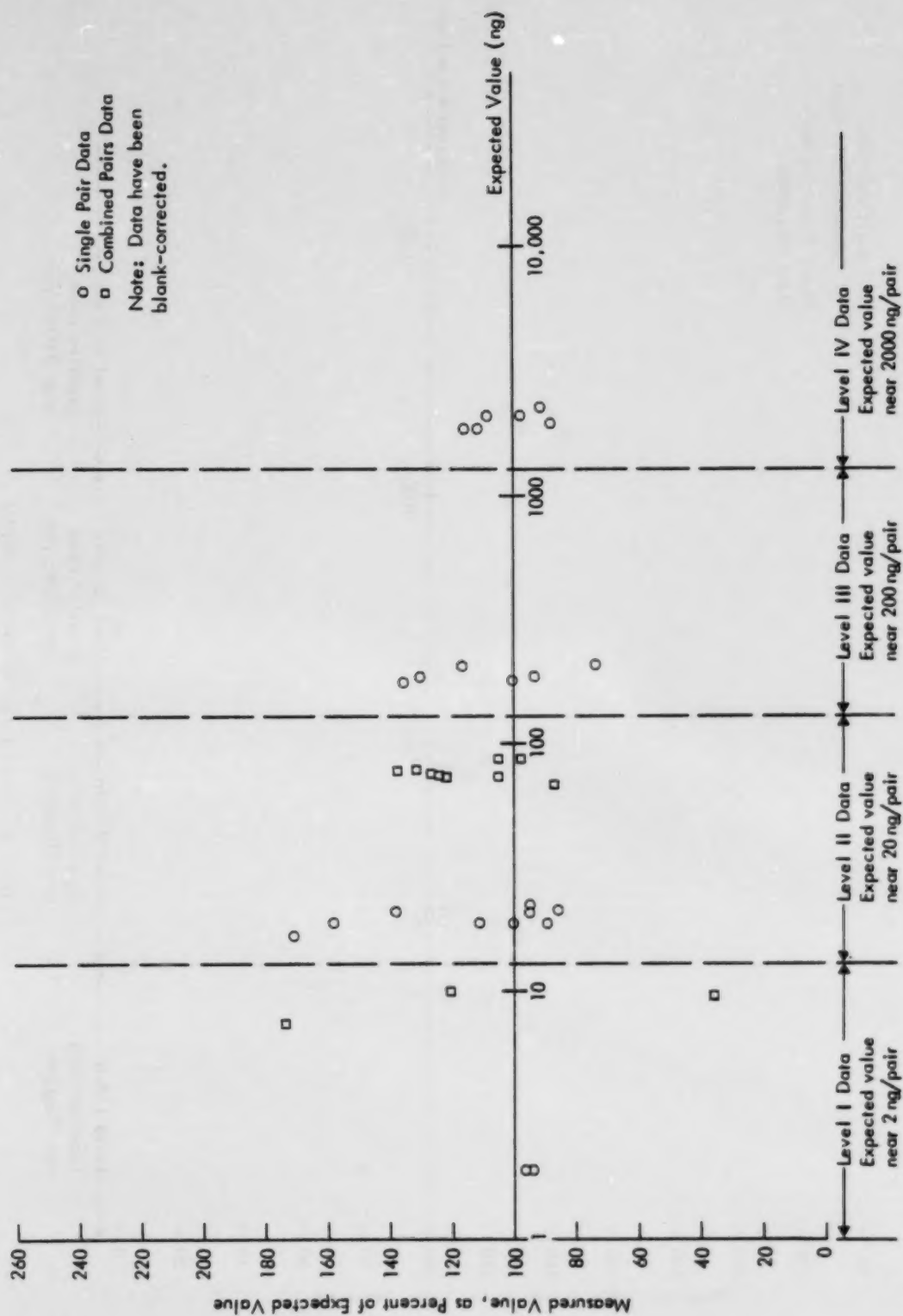


Figure 8. Chlorobenzene test results.

five pairs of traps each time, at 20 min each pair and a flow of 1-liter/min, the results from combining five pairs should be 10 ng. However, if the average for three tests (three runs) at this low concentration ranged from 50 to 150%, the reported value would be between 5 and 15 ng. As a result, the computed DRE would be:

Average amount detected	Computed DRE (%)
5	99.9995
10	99.9990
15	99.9985

In this first scenario it is clear that the sampling/analysis method does allow an accurate determination of DRE, and minimizes the need to report a DRE value as "greater than" 99.99% when it is actually achieving 99.999%.

As a second scenario, the situation might be that the waste again contains 100 ppm of another volatile POHC, but the incinerator is actually achieving a DRE of 99.99%. In this case, the amount of POHC present from combining five pairs of traps should be 100 ng. Since the average for three tests at this level may again range from 50 to 150% of the true value, the reported value might be as low as 50 ng or as high as 150 ng (i.e., $100 \text{ ng} \pm 50$). As a result, the computed DRE would be:

Average amount detected	Computed DRE (%)
50	99.995
100	99.990
150	99.985

From the above, it can be concluded that:

- The sampling/analysis method does provide assurance that the computed DRE is accurate to the same decimal place as the true DRE, even if the true DRE is as high as 99.999%.
- The computed DRE could be as low as 99.985% for an incinerator that is actually achieving 99.99%.

This second conclusion is vitally important since current regulations stipulate a DRE of 99.99%. Data obtained in this

project make it appear unlikely that a computed DRE would be below 99.985% for an incinerator that is actually achieving 99.99%.

4.0 DEVELOPMENT OF A FIELD VERSION OF THE VOST

Following the successful laboratory evaluation of the VOST described above, the VOST concept was chosen to be evaluated under field sampling conditions along with integrated gas bags. However, the laboratory version of the VOST was not deemed appropriate for field use for the following reasons:

- The difficulty in changing traps under field conditions.
- The lack of ruggedness of the sampling train.
- The high potential for contamination of the outside surfaces of the traps in the hostile environment of the stack and from handling the traps.

As a result of the need for a more rugged VOST with protected traps, several possible VOST and trap designs were considered and evaluated. This paper will only describe the final field version of the VOST which is being used at all trial burns conducted by MRI.

4.1 Trap Design

Figure 9 shows the various components of the field adsorbent traps used in the VOST. The following items should be noted.

- The dimensions of the glass tube remain the same except that neither end is nipped (10-cm x 1.6-cm ID glass tube).
- The amount of Tenax and Tenax/charcoal remains the same.
- The Tenax and charcoal are held in the tubes with a fine-mesh screen held by a C-clip both made from stainless steel. These supporting materials hold the adsorbents more uniformly inside the tubes than the glass wool used during the laboratory evaluation. This results in a lower likelihood of channeling

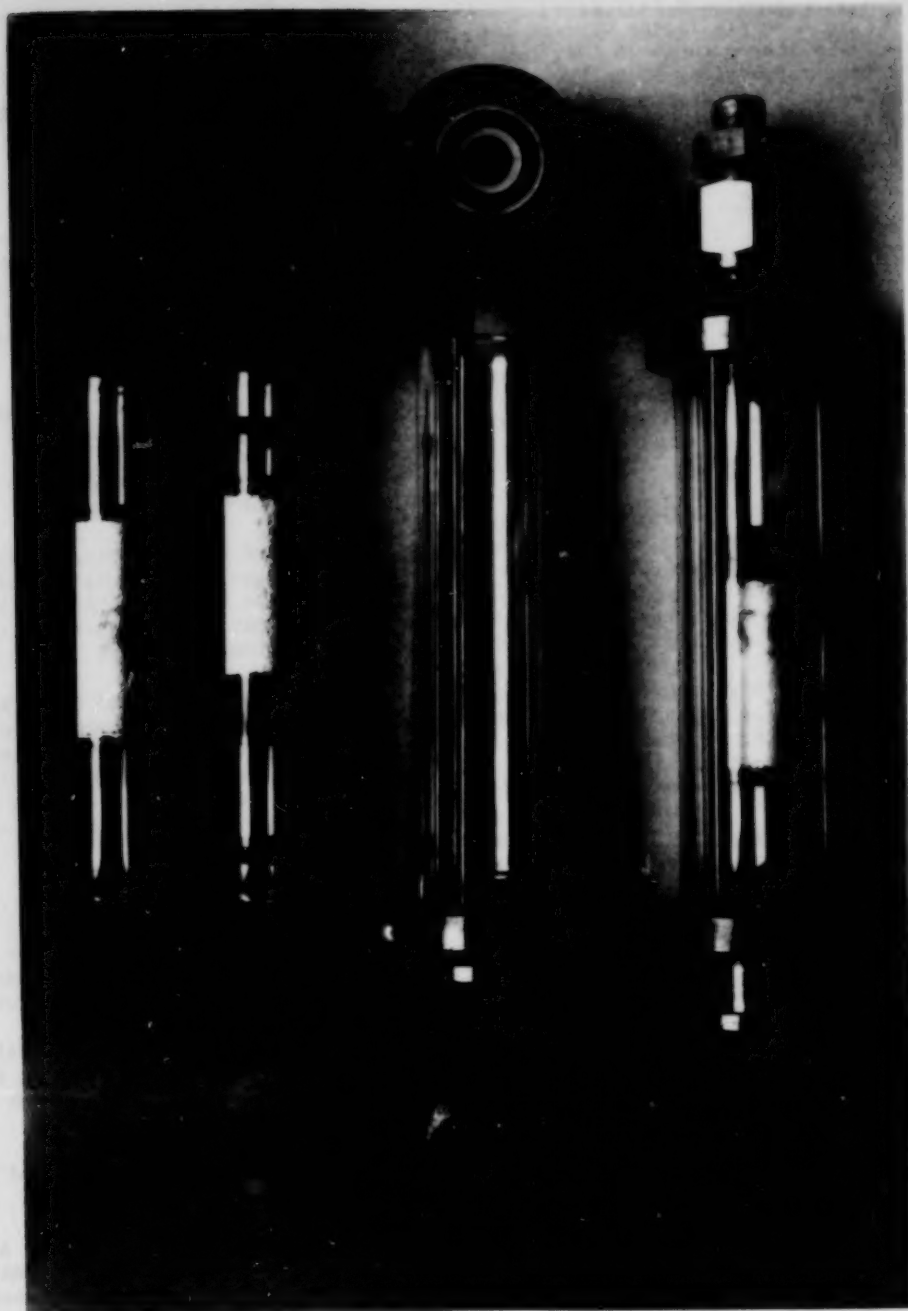


Figure 9. Components of field adsorbent traps for the VOST.

and lower retention of water in the trap. The stainless steel supports were found not to cause any degradation of volatile POHCs from thermal desorption during analysis.

- The glass tube containing the adsorbents is held within a larger diameter outside tube using Viton O-rings. The purpose of the outside glass tube is to protect the outside of the adsorbent-containing tube from contamination.
- The glass tubes are held in a stainless steel carrier. The glass tubes each butt up against Viton O-rings which are held in machined grooves in each metal end piece. A set of three cylindrical rods are secured into one of the end pieces and fasten to the other end piece with threads and nuts, thus sealing the glass tubes.
- The end pieces, which are fitted with a 1-in. (2.54 cm) female nut, are capped during transport and storage with an end-cap which also seals with a Viton O-ring.

4.2 VOST Design

A photograph of the field version of the VOST is shown in Figure 10. The uppermost section of glass tubing attaches to the probe which is inserted into the stack to collect the sample. The hot wet stack gases, which are drawn into the VOST by the air pump in the lower right-hand part of the photograph, are cooled in the first spiral condenser at the upper left. The bottom portion of the open case is filled with ice water which is continually circulated by a small water pump. The condensed water and stack gas then pass down through the front Tenax trap where most of the organics are adsorbed except those with very low breakthrough volumes; e.g., vinyl chloride. The condensed water collects in the Erlenmeyer flask-shaped impinger and is continually purged by the sampled gas. Any volatile POHCs which pass through the front Tenax adsorbent trap with the water are then purged from the water and pass upward through the Teflon® tube, down through the second spiral condenser and through the backup Tenax/charcoal trap where they are adsorbed. The gas is then dried in the silica gel tube and passes

into the dry gas meter for volume measurement. When not in use, the VOST folds up inside the portable case for easy transport.

The field VOST is generally used as described in the laboratory evaluation; i.e., one pair of traps is sampled for 20 min at a flow rate of 1 liter/min. The first trap pair is then removed and a new pair inserted for sample collection. A total of six pairs of traps are collected. The changing of the trap pairs is greatly facilitated by using the field carrier.

A "slow VOST" is also being evaluated during which only two or three pairs of traps are used for sample collection. The slow VOST, which generally samples only 5-10 liters of stack gas sample over a longer sampling period, has the following advantages:

- The lower sample volume reduces the likelihood of breakthrough and serves as a check on breakthrough for the regular VOST.
- A more integrated sample is obtained. This is very advantageous in situations where the stack gas composition changes during the incineration test.

The main disadvantage of the "slow VOST" is its decreased sensitivity.

4.3 Trap Preparation Procedures

During the development and evaluation of the field VOST, it was discovered that the sorbent traps were sometimes severely contaminated with volatile organic compounds. Several possible sources of contamination were identified such as ambient air, contaminated metal carriers, O-rings, and the adsorbents. In order to prevent contamination, a series of stringent trap preparation procedures were tested and adopted which have proved very effective in eliminating the contamination for field sampling with the VOST. These procedures are discussed below.

4.3.1 Preparation of Tenax and Charcoal--

New Tenax and charcoal is Soxhlet-extracted with methanol for 16 h, and dried in a vacuum oven at 50°C prior to packing into tubes. The Tenax and charcoal in

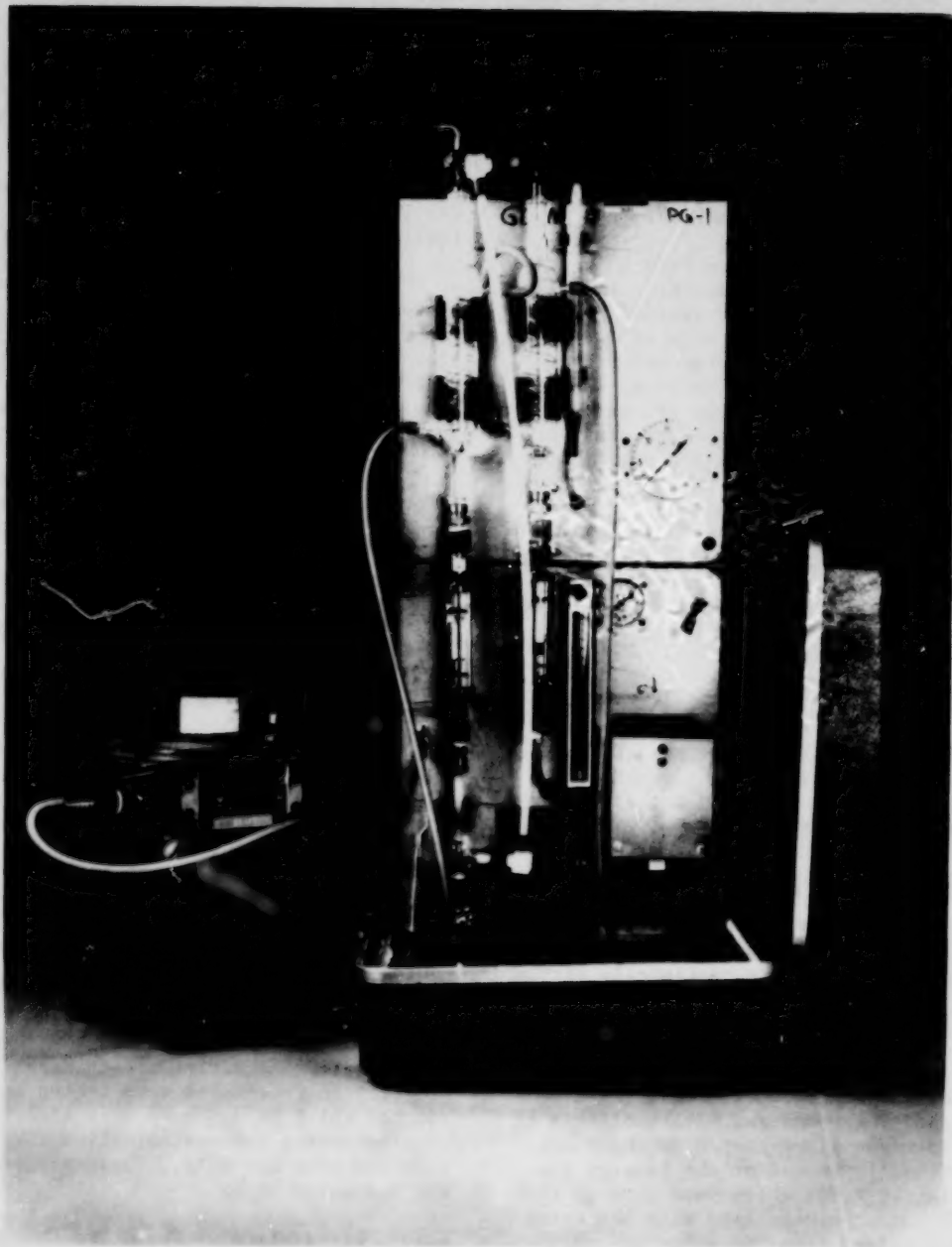


Figure 10. Photograph of the field version of the VOST.

packed tubes are not routinely reextracted following sampling and analysis unless very high concentrations (i.e., micrograms) of sample components are collected.

4.3.2 Preparation of O-Rings--

The Viton O-rings are thermally conditioned in a vacuum oven at 200°C for 48 h prior to use. This procedure removes volatile solvents which may be present in the O-rings and could outgas later.

4.3.3 Preparation of Metal Parts--

The metal parts (including the stainless steel carriers, end plugs, C-clips, and screens) are subjected to sonification in a warm non-ionic soap solution, rinsed with distilled water, air-dried, and heated in a muffle furnace at 400°C for 2 h.

4.3.4 Preparation of Glass Tubes--

The glass tubes are cut from new glass tubing, fire-polished, and annealed.

4.3.5 Packing--

The Tenax and charcoal are packed into the glass tubes in an organic-free laboratory (laboratory air filtered through charcoal).

4.3.6 Trap Conditioning--

The traps are conditioned as described in Section 3.4.3. However, two different conditioning periods are used of at least 4 h each.

4.3.7 Trap Assembly--

The conditioned traps are assembled into the metal field carriers in the same organic-free room where the adsorbents are packed into the glass tubes.

4.3.8 Leak Checking--

The assembled field traps are checked for leaks by removing one of the end caps and attaching the trap to a source of organic-free nitrogen gas at 30 psi (2.1 kg/cm²). The trap is then immersed in distilled water to check for the appearance of bubbles.

4.3.9 Trap Monitoring--

Following trap assembly and assurance that the traps do not leak, each trap assembly is attached to a manifold (capacity of 10 traps). Organic-free nitrogen is passed through each trap at a flow rate of 30 ml/min while the traps are heated to 190°C. The flow through each trap is sequentially monitored with a flame ionization detector to check for emission of volatile organics from the trap assembly. Most traps show no organic emissions, while others need to remain on the conditioner for several hours until the emissions from the trap are reduced to less than a detectable level (< 2 ppb).

4.3.10 Trap Storage--

When the traps are shown to be clean with the flame ionization detector, they are capped and stored under ice water until they are used for sampling. The traps are also placed back under ice water after sampling until they are analyzed by GC/MS. The ice water serves to keep the traps cold which slows aging of the Tenax; i.e., the gradual transfer of compounds such as benzene and toluene from within the polymeric Tenax matrix to the surface of the Tenax where these compounds can be thermally desorbed during analysis and contribute to high background levels. The water also protects the traps from volatile organic compounds in the ambient atmosphere which could collect on the outside of the trap assembly and contaminate the adsorbents during disassembly just prior to analysis. A summary of the trap preparation procedures is shown in Figure 11.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations based on this evaluation of the VOST are presented below. Some of the conclusions are preliminary and could change upon further evaluation of the VOST. We also expect that the precision and accuracy of the method will improve during further evaluation.

- This laboratory evaluation demonstrated that the overall concept for the VOST is valid, and that combining several pairs of traps onto one pair of traps for analysis is advantageous when the POHCs

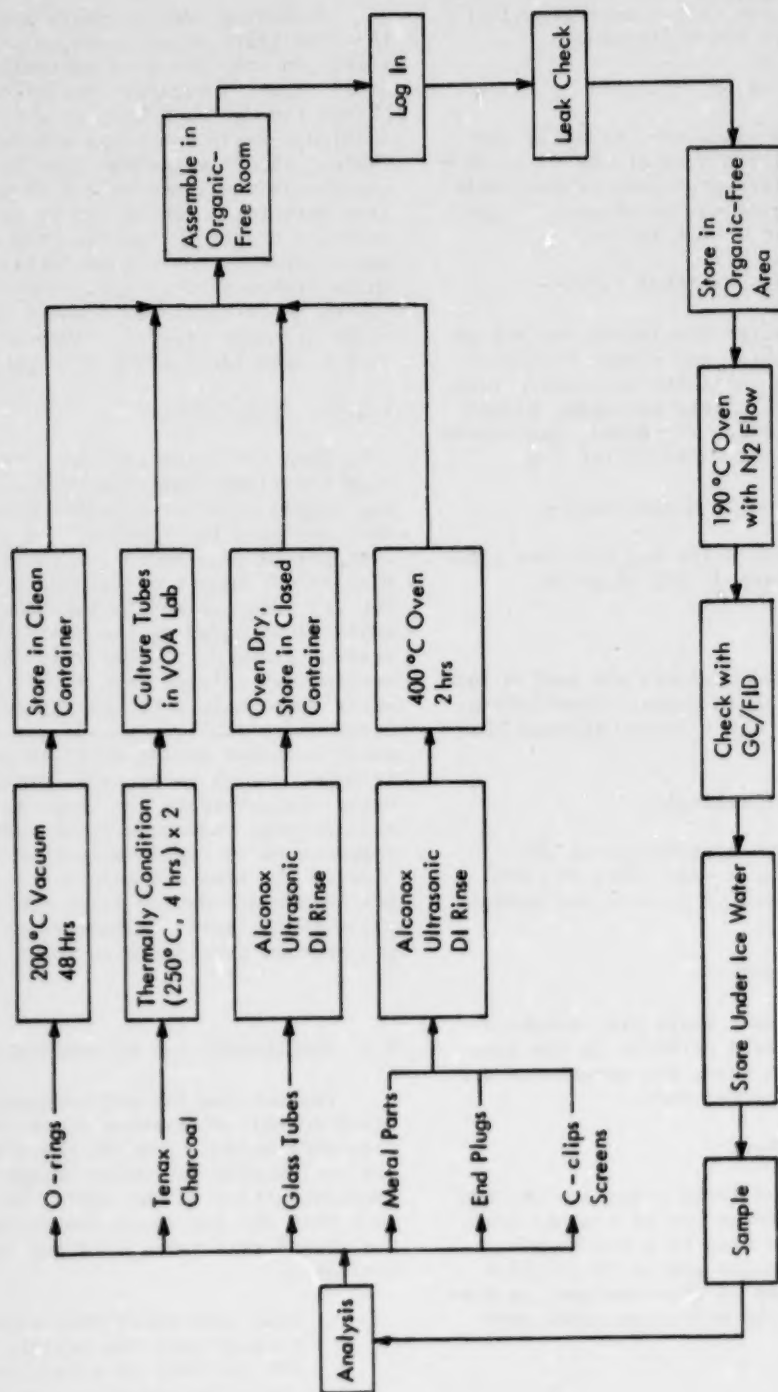


Figure 11. VOST trap cleanup procedure.

are present at low levels. The field work thus far, however, suggests that the levels of volatile POHCs are high enough that combining the contents of several pairs of traps onto one pair is generally not necessary.

- The VOST method does overcome the problem of reporting a DRE value of > 99.99% for an incinerator which is actually achieving 99.999%.
- Results of the laboratory evaluation indicate that a reported value may be as low as 46% or as high as 146% of the expected value (based on the average of three runs when several pairs from each sampling train are combined onto one pair).
- Therefore, for an incinerator that is achieving a DRE of 99.999% (100 ppm concentration of the POHC in the waste), the VOST method does permit determination of DRE to the third decimal place, but with results that could range from as low as 99.9985 to as high as 99.9995.
- The VOST method does not ensure that DRE results can always be accurately computed to the third decimal place. In fact, if an incinerator is actually achieving a DRE of 99.990%, the average results reported for three tests could have a deviation of $99.990 \pm 0.005\%$.
- In this evaluation, results for vinyl chloride and carbon tetrachloride show the most variability, especially at lower concentrations.
- The presence of HCl in the gas being sampled did not appear to have any serious effect on the VOST results.
- The problem of analyzing wet traps can be satisfactorily overcome by desorbing the contents of the sample collection traps into a purge-trap-desorb GC/MS analytical system.
- Stringent trap preparation procedures are required to eliminate the risk of contaminating the traps prior to use.

- Separate traps (blanks) should be exposed to air in the field in order to determine the level of compounds on the traps due to adsorption of the compounds during handling of the traps and their insertion into/removal from the VOST apparatus.

6.0 ACKNOWLEDGMENTS

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THE FEASIBILITY OF HYDRIDE GENERATION INDUCTIVELY
COUPLED PLASMA SPECTROSCOPY FOR ANALYSIS OF
VOLATILE METALS

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The detection limits normally obtained by inductively coupled argon plasma spectroscopy (ICAP) for arsenic, selenium, antimony, and mercury were reduced by factors of between 50-500 by use of a commercially available hydride generation system (Applied Research Laboratories). Coupling of the hydride generator to the spectrometer required minor modifications. Detection limits obtained in standard solutions of As, Se, Sb, and Hg were 0.2, 0.2, 0.1, and 0.2 $\mu\text{g/l}$, respectively. Analysis in some samples is difficult due to hydride suppression, particularly from aluminum and iron. Sample clean-up procedures can be used to eliminate some interferences.

INTRODUCTION

The method of inductively coupled argon plasma spectroscopy (ICAP) affords a rapid, accurate, and precise means for multielemental analysis of up to 70 elements in a wide variety of sample matrices. The detection limits obtained by this method are sufficient for most environmental studies, and the relative freedom from matrix interferences provides reliable quantitative analyses. However, the detection limits obtainable by the conventional pneumatic nebulizers commercially available are inadequate for some elements, specifically the Group IVA, VA, and VIA metalloids. Of particular concern in environmental analyses are low level determinations of arsenic, selenium, and antimony. Furthermore, detection of mercury at sub part-per billion levels is impossible by ICAP using pneumatic nebulization.

The method of hydride generation has been used for a number of years to determine sub-ppb levels of As, Se, and Sb when used in conjunction with atomic absorption spectroscopy (AAS). The application of the AAS method is relatively slow and expensive since a single element is analyzed during each run. Furthermore, an aliquot of 25-100 mL of sample is usually required for each determination,

thus limiting the technique to cases where large volumes of sample are available. Recently, hydride generation methods have been employed in conjunction with inductively coupled plasma spectrometers to provide rapid, multielemental ultratrace analysis of hydride-forming metals. Thompson et al (1) demonstrated the use of a prototype system and examined the effect of varying the acid media and optimizing the operating conditions for several elements. Robbins et al (2) examined the utility of a microwave induced plasma system for analysis of complex samples and found good recoveries in NBS orchard leaves when using the method of standard additions. The hydride generation-ICAP technique was applied to the analysis of arsenic, antimony, and bismuth in herbage after a dry ash procedure with magnesium nitrate (3). Wolnik et al increased the utility of the technique while decreasing the total analysis time per sample by designing a tandem nebulizer, permitting simultaneous introduction of the sample with a pneumatic nebulizer and with the hydride system (4).

The work conducted by these and other researchers demonstrated the feasibility and promise of the hydride ICAP technique. As a result, most ICAP manufacturers began

actively investigating the market potential of a commercial hydride generation unit designed specifically for ICAP use. This paper describes the set-up, interfacing, and application of a commercially available unit manufactured by Applied Research Laboratories, the first commercially available hydride generator produced for use with ICAP. The modifications required for interfacing to a different manufacturer's spectrometer are given. A comparison of results obtained using different acid media and the optimization of instrumental parameters are discussed. Preliminary interference studies, both from other hydride forming elements and from elements known to suppress the formation of hydrides in atomic absorption studies, are included.

EXPERIMENTAL SECTION

Spectrometer

The ICAP/polychromator used in this study was a Jarrell-Ash Model 975 Atom Comp, equipped for simultaneous analysis of 30 elements. For this study, results were taken from four channels; arsenic, selenium, antimony, and mercury. The spectrometer was equipped with the Spectrum-Shifter background correction capability. The argon coolant and sample flowmeters were replaced with mass flow controllers to provide more precise flow regulation.

Hydride Generator

The hydride generation system used was an ARL Model 341 Continuous Hydride Generator, manufactured in England. The system consists of a three head peristaltic pump, a sample and reagent mixing block, and a phase separator in which the liquid and gas phases are separated after reduction with the sodium borohydride.

In normal operation, the hydride generator works in the following fashion. A stream of sample is drawn into the mixing block by one channel of the peristaltic pump at about 6.0 mL/min. One reagent channel contains the sodium borohydride reagent which is mixed with the sample stream. The second reagent channel can contain hydrogen peroxide,

which is required for hydride determination of tin. In this study, the hydrogen peroxide stream was not required, rather deionized water was fed through this channel. Upon mixing with the sample, the sodium borohydride solution causes rapid formation of gaseous hydrides and excess hydrogen. The gases and the solution enter the phase separator, where the solution exits to a drain and the gases are swept into the ICAP torch via an argon carrier gas stream of approximately 1.0 L/min.

Mercury Determination

Although mercury does not form a hydride under the conditions generated, the reducing environment developed by the borohydride solution is sufficient to reduce mercury to the metallic state (5). The gas generated from the metallic mercury is swept into the plasma in a manner analogous to that used in cold vapor atomic absorption spectroscopy. Thus, an added benefit of the hydride generation procedure is the concurrent determination of mercury.

Reagents

Deionized water was obtained from a Barnstead Nanopure® system, with a reading of 15 M Ω or higher. The nitric, hydrochloric, and perchloric acids used were Baker Ultrex® grade. Sodium borohydride was obtained from Alfa Chemicals. A two percent w/v solution of borohydride was prepared and stabilized with a trace of NaOH. The solution was filtered through Whatman No. 1 filter paper prior to use. The borohydride solution was prepared fresh daily.

Hydride Generator Interfacing

The ARL Model 341 hydride generation system was designed to connect directly to the ARL line of ICAP spectrometers. Some modifications were required for use with the Jarrell-Ash Model 975 spectrometer system in our laboratories. First, the hydride unit is equipped with an interlock to prevent generation of hydrogen in the torch chamber if the torch is not lit. The interlock consists of an optical sensor which must be aimed directly at the ignited torch. If the torch is extinguished, the sensor immediately stops the peristaltic pump,

preventing the further generation of hydrogen. In the Jarrell-Ash spectrometer, the optical sensor was easily mounted inside the torch housing, immediately adjacent to the image focusing mirror. A small hole drilled in the mirror access door was used to pass the cable from the spectrometer to the hydride generation unit.

In order to transfer the hydride generated into the base of the torch, a special glass apparatus was designed. Originally, a length of tubing equipped with a glass ball joint was connected from the outlet of the generator to the base of the torch. However, in order to provide a stable mounting system, the device shown in Figure 1 was constructed. This apparatus consists of a glass transport tube connecting the hydride generator output to the base of the ICAP torch. The transport tube is surrounded by and attached to a glass housing which serves to support the torch assembly. This housing fits in the J-A holder for the expansion chamber used with the conventional pneumatic nebulizer. Thus, replacing the expansion chamber with the hydride transport system and connecting sample flow lines converts the ICAP from hydride to conventional. This interchange requires less than five minutes.

Initial work with the hydride ICAP system resulted in a poor signal to noise ratio for arsenic, and poor stability of the plasma itself. This problem was the result of a build up of pressure in the phase separator due to a blockage from excess liquid. In order to prevent this problem, the drain system was modified, incorporating a pressure by-pass system which prevents blockage of the phase separator. The by-pass system is shown in Figure 2. Once this system was in use, the plasma stability improved significantly, greatly improving the hydride ICAP performance.

Optimization

Optimum operating conditions were determined for the four elements selected (As, Se, Sb, Hg) by comparison of the signal to noise ratios obtained under each set of conditions. The parameters in the optimization procedure included the plasma gas flow rate, the carrier gas flow rate, the plasma forward power, and the lateral

and vertical torch positions. The optimum set of compromise conditions is given in Table 1, selected for maximum signal to noise for all four elements.

Acid Matrix Optimization

A brief literature search indicated an HCL matrix should be most suitable for multi-elemental hydride analysis. A preliminary study was conducted using 0.5 percent, 5 percent, and 10 percent HCL solutions as the matrix for the elements of interest. The best signal to noise was obtained with the 5 percent HCL solution for As, Se, and Sb. Initial studies indicated the HCL matrix was unsuitable for use with mercury, while a 5 percent HNO₃ matrix was reliable. However, once the pressure bypass system had been installed on the phase separator, stable determinations for mercury were obtained in a 1 percent HCL medium. This matrix was used for further studies. The instrument was calibrated using a blank and a single standard containing 200 ppb of all four elements of interest. Studies showed this to be near the upper end of the linear calibration range for all elements.

RESULTS AND DISCUSSION

Interelement Interferences

The instrument was calibrated as described above. Subsequently, single element solutions prepared at 200 ppb were run to determine whether interferences occurred for any of the remaining three elements. The results of this study are given in Table 2. These data indicate that no significant interelement interferences occur among these four elements, thus the simultaneous analysis of these four elements in solution by hydride generation ICAP is feasible.

Calibration Curve and Precision Studies

Standards were prepared containing all four elements over a concentration range of 5-200 ppb. The calibration curves were run on three separate occasions and the results for each element at each concentration were averaged. The average and relative standard deviations for the observed concentrations are given in Table 3. The low relative standard deviations obtained by these triplicate

determinations of mixed standards indicate the precise analytical capabilities of this method. Furthermore, a comparison of the observed average concentrations with the known concentrations indicate the accuracy of the technique in the ideal case, i.e. standards in 1 percent HCl.

A least square fit was performed on the data given in Table 3 for each of the four elements. The parameters describing the best fit line are given in Table 4 for each element. Note that the coefficient of correlation over the tested concentration range is 0.9998 or greater in all cases. Further, the y intercept is near zero in all cases. These data correspond to a linear dynamic range of at least 0-200 ppb. However, analysis of samples containing 200 ppb levels of the analytes has indicated that a long rinse time (>3 min) is required between samples to prevent carryover. Samples containing above 200 ppb can easily be analyzed by conventional pneumatic nebulizer ICAP.

The most frequently used method for reporting detection limits for ICAP is to calculate the analyte concentration giving a signal equivalent to three times the standard deviation of the blank. Based upon this convention, the detection limits obtained by the hydride generation-ICAP method are as given in Table 5.

Analysis of Complex Samples

Initial studies with complex samples have concentrated on the analysis of fly ash samples. Unfortunately, significant interferences eliminated the possibility of conducting the analyses. High levels of aluminum, iron, and/or copper in the samples are suspected to be the primary source of interference. It should be noted that these elements routinely cause significant suppression of the hydride signal obtained in atomic absorption, and the method of standard additions is frequently required for these determinations. Future work here will examine potential clean-up steps to eliminate the requirement for use of standard addition methods.

The most promising cleanup technique is the use of a cation exchange resin to remove the interfering elements from solution prior to hydride generation-ICAP analysis of the sample. In a recent paper,

Jones et al (6) described the use of Chelex 100 resin to clean up samples prior to analysis by hydride generation atomic absorption. At pH of 5.3, they found that most metals were retained on the resin, while the metalloids passed through the resin bed quantitatively, thus the interfering elements were removed easily. Earlier work in our laboratories on sea water agrees with this finding. Future work will include application of the Chelex 100 resin cleanup procedure to samples of various types, including industrial effluents and incinerator byproducts.

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DISCLAIMER

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SPECIATION OF HALOGEN AND HYDROGEN
HALIDE COMPOUNDS IN GASEOUS EMISSIONS

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ABSTRACT

A sampling and analytical method for the speciation and quantification of hydrogen halide (HX) and halogen (X₂) emissions in a gas stream was evaluated in the laboratory. Analyte gases of certified purity were introduced into a mixing and sampling manifold system, dynamically diluted with air, and sampled into a series of midget impingers. Quantification of analyte species was performed by ion chromatography. The methodology was also evaluated in the presence of SO₂ and NO_x matrix gases. The procedures were effective in selectively absorbing HX and X₂ from the gas stream providing for the speciation of these gases.

INTRODUCTION

The proper disposal of hazardous waste is one of the important environmental problems of this decade. In order to address this issue, the United States Congress passed the Resource Conservation and Recovery Act (RCRA) in 1976 which empowered the Environmental Protection Agency to promulgate regulations concerning the management of hazardous waste. To this end, the EPA established standards for waste generators, transporters, and operators of hazardous waste facilities (40 CFR 260-267).

Of the waste disposal methods presently employed, incineration is emerging as a means of ultimate disposal in a safe, cost-efficient, and environmentally sound manner [Bonner (1)]. However, an incinerator burning hazardous waste must achieve a destruction and removal efficiency (DRE) of 99.99% for each principal organic hazardous constituent (POHC) designated in its permit. Moreover, if the waste contains more than 0.5% chlorine, then 99% of the hydrogen chloride produced during incineration must be removed from the exhaust gas (40 CFR 264). To demonstrate compliance with these regulations, sampling and analytical methods which can quantitate POHCs and HCl emissions are required.

Substances classified as hazardous (Appendix VIII, 40 CFR 261) encompass a wide variety of materials having a correspondingly wide range of combustion characteristics. This often results in incinerator emissions that are substantially different from site to site and from burn to burn. Of the 375 constituents listed in Appendix VIII, about 100 (or nearly 27%) contain chlorine. Additionally, 12% of the Appendix VIII constituents contain sulfur and 39% contain nitrogen. Thus, when these materials are combusted, a complex gas stream will be produced which will likely contain both SO_x and NO_x.

Analytical methods for halogen compounds have not been critically evaluated in this matrix nor have they been designed to permit speciation. As shown in Table 1, the methods commonly used for measurement of halogen species are not analyte specific and are therefore prone to significant bias. For example, in the determination of chlorine by the o-tolidine colorimetric method, serious positive errors will occur if bromine, ozone, or other oxidizing agents are present in the gas stream [Ruch(4)]. The matrix gas, SO₂, will drastically mask the end point in the mercuric nitrate titration of chloride (for HCl) causing positive errors of 100 fold [Cheney and Fortune (2)].

TABLE 1. COMMON METHODS FOR HALOGEN/HALIDE ANALYSIS

Analyte	Absorbing Solution	Sampling Rate	Method	Interferences
Cl ₂ , Br ₂	NaOH	1 lpm	Colorimetric	ClO ₂ , most oxidizing agents (OA)
Cl ₂ , Br ₂	KI	1 lpm	Colorimetric	ClO ₂ , OA
HX	H ₂ O	1 lpm	Potentiometric, Volumetric, Turbidimetric	Other halides present
HX	NaOH	1-3 lpm	Potentiometric, Volumetric	Other halides present; other acidic gases (SO ₂ , H ₂ S)

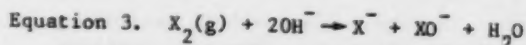
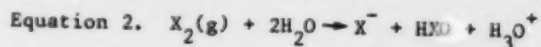
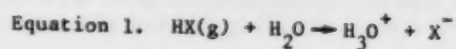
The purpose of the investigation reported here is to develop and evaluate a sampling and analytical scheme for halogen and hydrogen halide speciation and quantification that can be applied to incinerator flue gas streams. The effects of SO_x and NO_x as matrix components are investigated.

EXPERIMENTAL PROGRAM

A computer search of the literature indicated that a simple sampling scheme did not exist for the speciation and quantification of inorganic halogen compounds. Therefore, we endeavored to design and develop a sampling and analytical procedure which could quantitate HCl, HBr, Cl₂, Br₂, and HF and perhaps other analytes, such as HCN, in process streams typical of hazardous waste incinerators.

Sampling Train

The sampling train proposed to absorb and speciate these compounds is shown in Table 2. It consists of 4 midget impingers connected in series; the first two impingers contain water and the last two contain sodium hydroxide solution. Initial calculations and theoretical considerations suggested that HF, HCl and HBr would be absorbed in water with Cl₂ and Br₂ collected in sodium hydroxide. The chemical reactions occurring in the impingers are shown below:



Reactions 1,3 have large equilibrium constants favoring analyte absorption and halide formation in the specified impingers. Cl₂(aq) and Br₂(aq) do not react favorably with water (K_{eq} of 10⁻⁴ and 10⁻⁹, respectively) but rather remain as the aquated species. Therefore, it was anticipated that clean air purging would reduce their concentrations in water to minimal levels and effectively drive these analytes into the sodium hydroxide impingers.

Quantification

To minimize sample handling and contamination, a technique was required which was capable of accurate and reproducible measurements and which had ppm sensitivities to the analytes. Because ion chromatography (IC) meets these requirements and has multiparameter capabilities, it was the technique of choice. Interferences normally caused by species simultaneously collected in the impingers are either eliminated or minimized by the high degree of resolution achieved by the chromatographic column [Holm (3)].

TABLE 2. PROPOSED SAMPLING TRAIN

	Impinger #1	Impinger #2	Impinger #3	Impinger #4
Absorber	H ₂ O	H ₂ O	NaOH(0.1M)	NaOH(0.1M)
Analytes Collected	HCl, HBr, HF	HCl, HBr, HF	Cl ₂ , Br ₂	Cl ₂ , Br ₂
Other Species of Interest	SO _x , NO _x	SO _x , NO _x	SO _x , NO _x	SO _x , NO _x
Analytical Finish	ION CHROMATOGRAPHY			

All analytical determinations for F⁻, Cl⁻ and Br⁻ were performed on a Dionex Model 14 Ion Chromatograph (Dionex Corp., Sunnyvale, CA). Normal operating procedures employed an anion separator column and a fiber suppressor with conductivity detection. The eluent was 0.003 M NaHCO₃ and 0.0024 M Na₂CO₃ at a flow rate of 2.3 ml/min. Part per million (ppm) sensitivities were easily obtained.

Procedure

To evaluate the proposed sampling train and analytical finish for its ability to differentiate and quantitate the halogen/halide species, a laboratory investigation was performed. Each gaseous analyte was introduced into an all glass manifold system (Figure 1), diluted with clean/dry laboratory air, sampled using midget impingers, and analyzed by IC. Analyte combinations at different concentrations with and without a matrix gas background of SO₂ and NO_x were also investigated. Gas sampling into the midget impinger train was performed at either 0.50 lpm or 1.00 lpm for 30 minutes using calibrated rotameters for flow control. Using slightly higher sampling rates, although possible, ran the risk of carry over and impinger stem blow out and were therefore not used in this study.

Materials

Analyte gases of HCl, HBr, and Cl₂ were custom blended by Matheson Gas Products (Gloucester, MA) as dilute

mixtures in nitrogen. Their concentrations were 1.04%, 0.083%, and 0.075% (v/v) respectively. Custom blended matrix gases of SO₂ (1.59%) and NO_x (4.82% NO, 0.05% NO₂) in nitrogen were used to simulate matrix background effects (Matheson Gas Products).

Corrosion resistant gas regulators and flow meters (Matheson Gas Products) were used in all cases. To minimize analyte gas adsorption, connections between gas cylinder, manifold, and impingers were made with Teflon tubing (1/4" o.d.). Diluent air was laboratory compressed air passed through Drierite and activated carbon prior to introduction into the manifold. All reagents used in this study were ACS reagent grade or better. The high purity water was equivalent to ASTM Type I water.

RESULTS AND DISCUSSION

Prior to using the manifold system, a series of preliminary tests were performed to determine qualitatively the clean air purging efficiency of Cl₂ and Br₂ from water impingers. Four Greenburg-Smith impingers were connected in series; the first two contained water, and the last two contained sodium hydroxide. The first impinger was spiked with bromine liquid to produce concentrations of either 1,10 or 100 mg/l. After 20 minutes of clean air purging at 500 ml/min (0.5 lpm), the impinger solutions were tested for the halide anion using silver nitrate solution. Similar experiments were performed using chlorine-water in the first impinger.

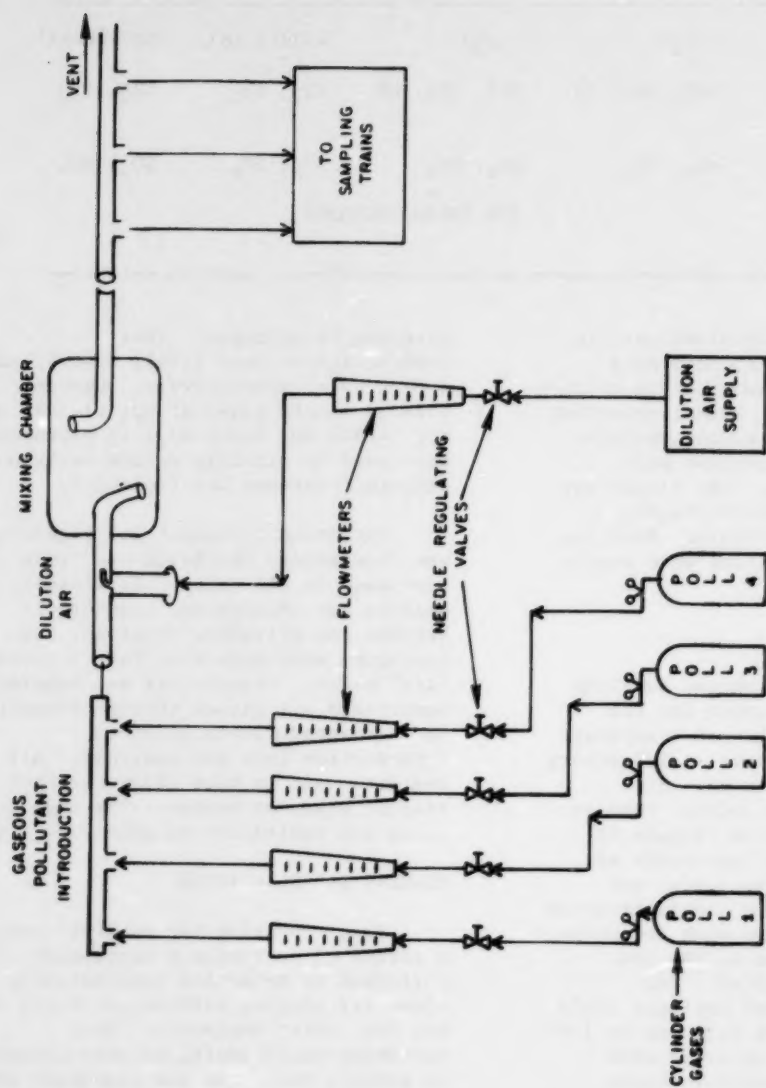


Figure 1. Mixing and sampling manifold system.

In each case, the free halogen will form the halide and the hypohalite ions which should precipitate upon addition of AgNO_3 . In the NaOH impingers, the pH was adjusted to approximately 8.0 by addition of concentrated nitric acid to prevent precipitation of the hydroxide as AgOH and thus possibly confound the results. No adjustments were necessary in the water impingers. Table 3 shows the results for these trials.

These preliminary results which suggested successful clean air purging were sufficiently encouraging to warrant proceeding with more definitive testing. Individual test streams of HCl/air , HBr/air , and Cl_2/air were generated by metering these analytes from gas cylinders of certified concentration into the glass mixing and sampling manifold system (Figure 1). The analytes were dynamically diluted to the desired concentration by introducing clean, dry laboratory air. For example, an HCl test stream of 130 ppm (v/v) was generated by metering in 10,400 ppm HCl (in nitrogen) at 0.050 lpm with air dilution at a rate of 3.95 lpm. Total test stream flow was therefore 4.00 lpm.

The analytes in question were sampled at 0.50 lpm and 1.00 lpm into a series of midjet impingers. Impingers 1 and 2 each contained 15 ml of water, and impingers 3 and 4 each contained 15 ml of 0.10 M NaOH . All analytical determinations were performed by ion chromatography.

Excellent overall recoveries were obtained for HCl/air and Cl_2/air test atmospheres (Table 4), demonstrating the combined ability to generate and quantitate these process streams. HBr/air streams demonstrated poor recoveries suggesting other forces at work; surface adsorption, sample degradation, analytical anomalies.

As shown in Table 4, significant amounts of residual chlorine remained trapped in the water impingers. Concentrations of chloride after 30 min of purging, T_{30} , showed no difference relative to T_0 . This experiment was repeated several times to confirm the "non-purging" phenomenon. Table 5 presents absorption efficiency data for HCl . For these stream concentrations,

99.8% of the HCl is collected in the first water impinger.

A calculation of the chlorine collection efficiency, for Cl_2/air gas streams, revealed that the water impingers collected 37% (average, $n = 4$) of the chlorine whereas the alkaline impingers absorbed 63% as summarized in Table 6. Clearly, for speciation purposes this distribution appeared to preclude the use of this sampling train system. However, from an examination of Equation 2, it is expected that the disproportionation of Cl_2 , and hence its solubility in water would be significantly repressed in low pH media. This suggested that lowering the pH of the aqueous medium would result in more favorable Cl_2 purging. In a typical application, e.g., incineration, the gas stream will probably contain high levels of HCl . Therefore it was expected that HCl extant in the flue gas would serve to enhance the speciation both by lowering the pH and by common ion and mass action effects.

To test this hypothesis, a gas stream containing 260 ppm HCl and 19 ppm Cl_2 (in air) was generated and sampled according to procedures previously discussed. The results for two independent trials are shown in Table 7. The theoretical amounts were calculated assuming all of the generated HCl was collected in water impingers (1 and 2) and all of the generated Cl_2 was purged out of water and absorbed in the sodium hydroxide impingers (3 and 4). The somewhat high chloride content (~118% recovery) found in the water impingers was not surprising and most probably reflected the uncertainties of the HCl rotameter. The Cl_2 recoveries of 81% and 68% indicated fair speciation efficiency.

Further inspection of the data shows impinger collection characteristics which provided for even better speciation efficiency. Since essentially 100% of the HCl is collected in the first water impinger (Table 5), it is proposed that the chloride found in the second impinger originated from Cl_2 and not from HCl . Because the pH of this water impinger was found to be 4 (as opposed to pH 1 in the first water impinger), it is expected that clean air purging will not be as

TABLE 3. HALOGEN SPARGING EFFICIENCY

(Bromine concentration of 1.0 mg/l in impinger No. 1
sparged for 20 min at 500 ml/min)*

	Impinger #1	Impinger #2	Impinger #3	Impinger #4
Absorber	H ₂ O	H ₂ O	NaOH	NaOH
Color				
Initial	Orange	Colorless	Colorless	Colorless
Final	Colorless	Colorless	Colorless	Colorless
AgNO ₃ Test	Negative	Negative	Positive	Positive

*Similar results were obtained using 10 and 100 mg/l Br₂ and 1, 10, and 100 mg/l Cl₂.

TABLE 4. ANALYTE RECOVERIES FROM PROCESS STREAMS

Run	Analyte	Stream conc. ppm (v/v)	Sampling rate, lpm	Sampling time, min	Theoretical µg analyte generated*	µg Collected*				Total	% Recovered
						Imp #1 H ₂ O	Imp #2 H ₂ O	Imp #3 NaOH	Imp #4 NaOH		
1	HCl	130	1.0	30	5640	5570	8	ND	ND	5578	99
2	HCl	130	1.0	30	5640	5430	22	ND	ND	5452	97
3	HCl	130	0.50	30	2820	2805	8	ND	ND	2878	102
4	Cl ₂	19	1.0	30	826	234	110	459	21	824	100
5	Cl ₂	19	1.0	30	826	228	114	558	13	913	110
6	Cl ₂	19	1.0	30	826	176	88	635	20	919	111
7	Cl ₂	19	0.50	30	413	110	65	240	21	436	106
8	HBr	10	1.0	30	980	116	8	ND	ND	124	13
9	HBr	10	0.50	30	490	45	4	ND	ND	49	10

ND = not detected

* = expressed in terms of the halide anion

TABLE 5. IMPINGER ABSORPTION EFFICIENCY FOR HCl

HCl stream concentration ppm	Percent HCl absorbed			
	Imp #1 H ₂ O	Imp #2 H ₂ O	Imp #3 NaOH	Imp #4 NaOH
130	99.9	0.1	0	0
130	99.6	0.4	0	0
130	99.7	0.3	0	0
800	99.9	0.1	0	0
Ave.	99.8	0.2		

TABLE 6. WATER AND SODIUM HYDROXIDE SCRUBBER EFFICIENCY FOR Cl_2^*

	$\mu\text{g Cl}^-$ Collected (% collected)				
	Run Number				
<u>Impingers</u>	4	5	6	7	Ave %
H ₂ O	344 (42)	342 (37)	264 (29)	175 (40)	37
NaOH	480 (58)	571 (63)	655 (71)	261 (60)	63
Total (found)	824	913	919	436	
Total (theoretical)	826	826	826	413	

* Cl_2 concentrations in gas stream was 19 ppm.

TABLE 7. HCl/Cl_2 SPECIATION EFFICIENCIES*

	$\mu\text{g Cl}^-$			
	Combined Water impingers (1+2) (HCl)		Combined Sodium hydroxide impingers (3+4) (Cl_2)	
	Trial 1	Trial 2	Trial 1	Trial 2
Found	13,980	13,670	685	575
Theoretical**	11,700	11,700	851	851
% Collected	119	117	81	68

* HCl and Cl_2 stream concentrations were 260 and 19 ppm (v/v) respectively.

**Calculated amounts assuming complete speciation.

effective in driving out the chlorine from this impinger. Using chloride data from impingers 2, 3, and 4 to calculate Cl_2 recovery resulted in an average speciation of 95% as seen in Table 8. This supports the hypothesis that some Cl_2 remains in impinger 2.

However, because the carryover of HCl from impingers 1 to 2 and thus the resultant acidity of impinger 2 cannot be predicted with great certainty, this method of calculation is not recommended. To circumvent this apparent drawback and to further investigate the effect of pH on Cl_2 solubility and speciation

efficiency, it was decided to acidify impingers 1 and 2 with H_2SO_4 to pH ~1 prior to sampling.

In addition, SO_2 and NO_x gases were introduced into the process stream to document the speciation of HCl/Cl_2 when these matrix gases are present. Table 9 shows the distribution of the SO_2/NO_x matrix gases, present as dissolved anions, in the impinger train. Quantification of these species was not necessary but it was apparent from inspection of the ion chromatograms that SO_2 produced sulfate and lesser amounts of sulfite, whereas, NO_x formed mostly

TABLE 8. HCl/Cl₂ SPECIATION EFFICIENCY*

		μg Cl ⁻				
		Imp #1 H ₂ O	Imp #2 H ₂ O	Imp #3 NaOH	Imp #4 NaOH	Total(2,3,4)
Found	Trial 1	13,800	182	675	11	868
	Trial 2	13,500	165	570	5	740
Theoretical		11,700**		851**		
% Collected	Trial 1	118				102
	Trial 2	115				87 (ave., 95)

*HCl and Cl₂ stream concentrations were 260 and 19 ppm (v/v), respectively, and sampled at 1 lpm.

**For HCl and Cl₂ respectively.

TABLE 9. MATRIX GAS SPECIE DISTRIBUTION FOR SO₂ AND NO_x*

Impinger #1 (H ₂ O)	Impinger #2 (H ₂ O)	Impinger #3 (NaOH)	Impinger #4 (NaOH)
SO ₄ ²⁻	NO ₂ ⁻ , SO ₃ ²⁻ , NO ₃ ⁻ , SO ₄ ²⁻	NO ₂ ⁻ , NO ₃ ⁻ SO ₄ ²⁻	NO ₃ ⁻ , SO ₄ ²⁻

*SO₂ and NO_x stream concentrations were 250 and 600 ppm, respectively.
HCl and Cl₂ stream concentrations were 530 and 19 ppm, respectively.

nitrite and some nitrate. Using a "slow" anion separator column, excellent resolution of analyte species was achieved.

Table 10 demonstrates the speciation efficiency for HCl/Cl₂ with prior acidification of impingers 1 and 2 in the SO₂/NO_x matrix. As expected, differentiation between HCl and Cl₂ species was successful. In this trial excellent recovery of HCl and Cl₂ was achieved with 99.4% of the HCl collected in the first impinger. The slightly high recoveries of HCl and Cl₂ resulted from small fluctuations in the rotameter float positions which permitted larger actual flow rates of these gas species.

In summary, it has been shown that it is possible to differentiate between HCl and Cl₂ species in a laboratory-generated air stream. The next phase of this project should be carried out using a combustion gas stream with a gas-particle separator to determine their effects on the separation and analysis. For effective speciation using this absorption train, it is important that the water impingers should be acidified to pH 1 prior to sampling. The major components of most process streams are SO₂ and NO_x and these gases, as demonstrated in this work, do not interfere with the ion chromatographic determinations.

TABLE 10. HCl/Cl₂ SPECIATION EFFICIENCY IN SO₂/NO_x STREAM*

	µg Cl ⁻			
	Impinger #1 (H ₂ O, pH ~1)	Impinger #2 (H ₂ O, pH ~1)	Impinger #3 (NaOH)	Impinger #4 (NaOH)
Found	28,100	160	735	173
Theoretical	23,000		826	
% Collected	123		110	

*HCl and Cl₂ stream concentrations were 530 and 19 ppm, respectively.
SO₂ and NO_x stream concentrations were 250 and 600 ppm, respectively.

DISCLAIMER

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DIOXIN COLLECTION FROM HOT STACK GAS
USING SOURCE ASSESSMENT SAMPLING
SYSTEM AND MODIFIED METHOD 5
TRAINS--AN EVALUATION

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ABSTRACT

Dynamic gas-phase spiking was used to demonstrate the collection efficiency of two EPA source sampling systems for tetrachlorodibenzo-p-dioxins. The Source Assessment Sampling System and Modified Method 5 trains were used to collect a representative sample administered in trace quantities into the hot exhaust gas from a flue gas source capable of simulating incinerator stack conditions. Nine experiments were performed with the two sampling systems to measure the overall method recoveries for varied levels of 1,2,3,4-tetrachlorodibenzo-p-dioxin. High resolution glass capillary column gas chromatography/high resolution mass spectrometry techniques were used to analyze the collected samples. Recoveries were considered quantitative for all spiking experiments, except one, demonstrating the usefulness of the SASS and MM5 trains in collecting and analyzing low levels of dioxins in hot, gaseous combustion emissions.

INTRODUCTION

It is critical, in measuring trace quantities of organic species in combustion gas streams, to use well documented procedures that have been evaluated for specific applicability to the source studied. Since the analytical process must begin with sampling, defensibility of any combustion stream study requires appropriate quality control checks at every stage in sample taking and sample handling.

In this study two sampling systems were chosen for evaluation as research tools to measure combustion flue gas, the Source Assessment Sampling System (SASS) train and the Modified Method 5 (MM5) train. These two EPA sampling systems have been used in sampling many source types (1-2).

In this study the two sampling systems, SASS and MM5, were challenged with low levels of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) in the gaseous discharge of a gas-fired research combustor. Generating a continuous flue gas stream which contains known levels of a test compound is a challenging task. The flue gas tested must be taken from an authentic source discharge, and the spiking system for administering the compound of interest must ensure complete mixing in the gas stream and must, in its design, prevent deposition or decomposition.

This paper describes a study designed to spike hot flue gas with low levels of 1,2,3,4-TCDD, collect the spiked flue stream using two standard sampling systems, then measure the overall recovery by a high resolution gas

chromatography/high resolution mass spectrometry (HRGC/HRMS) technique. The goal of this study was to determine the efficiency of collecting and retaining low levels of dioxins from combustion discharges. Richard and Junk (3) described a dynamic injection system for spiking an incineration flue stream with a polychlorinated biphenyl standard. Recently Petersen *et al.* (4) described an experiment to spike a hot diesel engine exhaust stream with perdeuterated polynuclear aromatic hydrocarbon (PAH) standards to determine if a significant loss of PAH occurred during sampling and analysis.

In this study low levels of 1,2,3,4-TCDD were continuously administered into the hot flue gas stream at a range of concentrations which simulated the low level discharges reported in the literature on incineration. Overall recovery of 1,2,3,4-TCDD was used to assess the efficiency of the two EPA source sampling systems to collect, retain, and stabilize ultra-trace TCDD levels for subsequent analysis.

TEST STRATEGY

A pilot plant furnace was used to generate the simulated incinerator flue gas. A low flow rate pump was used to inject a TCDD sample solution into a slipstream of the flue gas where the gas temperature was approximately 260°C (500°F). Flue gases were then sampled by the stack sampling equipment. The sampling temperatures, rates, and volumes were typical of those used in a MM5 or SASS apparatus. Since TCDDs are highly toxic compounds, it was imperative that none of the sample escaped into the environment. To prevent such emissions, all gases spiked with 1,2,3,4-TCDD were passed through the sampling train followed by a charcoal filter trap used as a secondary filter. A schematic diagram (Figure 1) shows the experimental setup: natural gas combustor outlet; hot gas spike injection; sampling train; charcoal safety filter; and gas moving system.

COMBUSTION AND SAMPLING SYSTEMS

In this program, two sampling trains (SASS and MM5) were used. The SASS

equipment was operated in accordance with procedures outlined in the EPA Level 1 manual (5). Because a relatively clean fuel (natural gas) was used to produce the flue gas stream sampled, some modifications were made to the standard SASS apparatus. The normal stack sampling probe and cyclones were replaced with borosilicate glass connecting tubing. Since the flue stream was essentially particulate free, the stainless steel cyclones were removed. The solutions that would normally be contained in impingers 1 and 2 were eliminated, although the impingers were left in the system as condensate traps. Impinger 3 contained a charge of activated charcoal to serve as a safety filter in the event that 1,2,3,4-TCDD escaped collection in the resin bed. Impinger 4 contained a charge of silica gel to protect the sampling pumps and dry gas meter. The modified SASS sampling apparatus is illustrated in Figure 2.

The major difference between the SASS and MM5 trains is in the sampling rate and volume of gas collected. This gas volume allows the use of a smaller quantity of XAD-2 in the MM5 train. The filter is typically held at a higher temperature in the SASS train. The MM5 train and location of gas-phase spiking are shown in Figure 3.

A development of this study was a gas-phase spiking system that could inject liquid solutions of the test material into the hot flue gas stream. A fused silica capillary line was used to transfer the dioxin solution from a precision metering pump to the flue gas stream. Condensation was prevented by jacketing the capillary at the point where heating occurred. By circulating a refrigerant around the transfer line up to the point where the capillary discharged into the hot flue gas, premature vaporization and condensation were prevented. The primary solvent was acetone with a keeper, 0.5 percent (v/v) decane, added in order to wet the final segment of transfer line and prevent deposition of the small amount of 1,2,3,4-TCDD in the capillary tip.

As shown in Figure 4, a slipstream was drawn from the primary combustion discharge into the sampling apparatus. The transfer line in which solution spiking occurred was insulated and

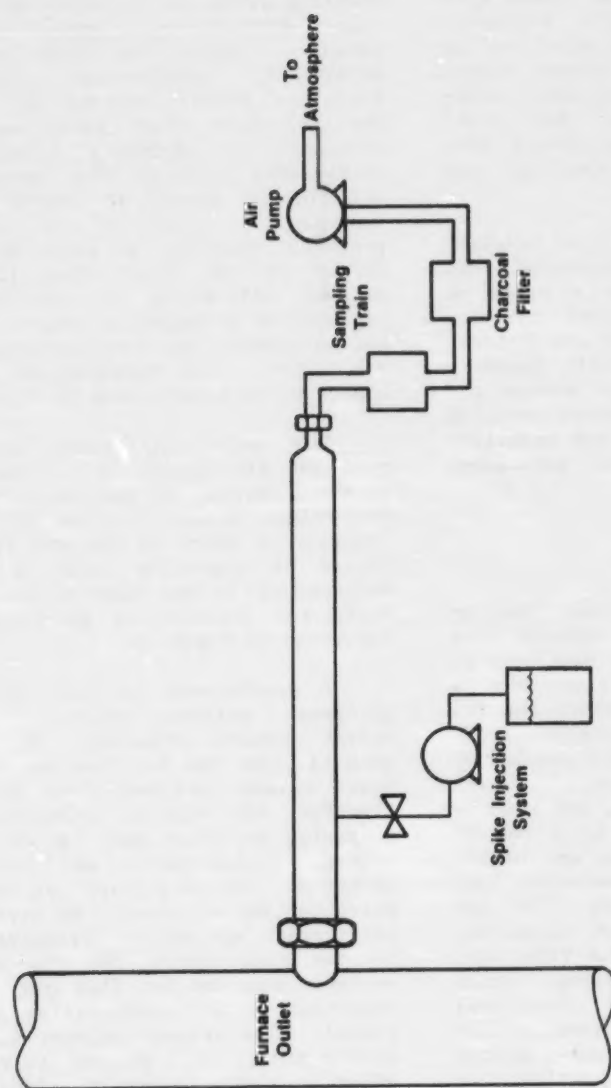


Figure 1. TCDD Injection and Sampling Apparatus.

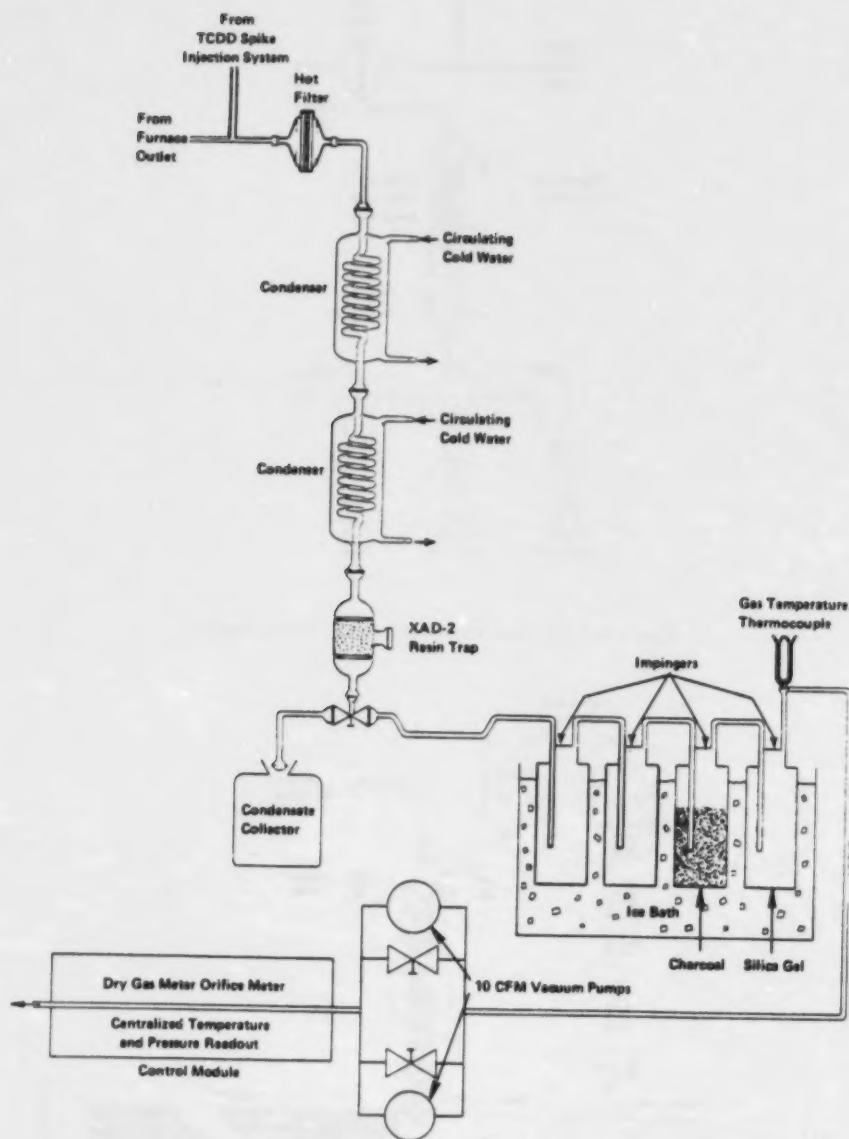


Figure 2. Source Assessment Sampling System (SASS).

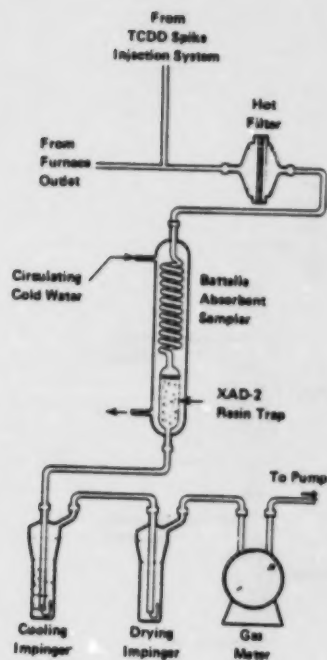


Figure 3. Modified Method 5 Sampling System (MM5).

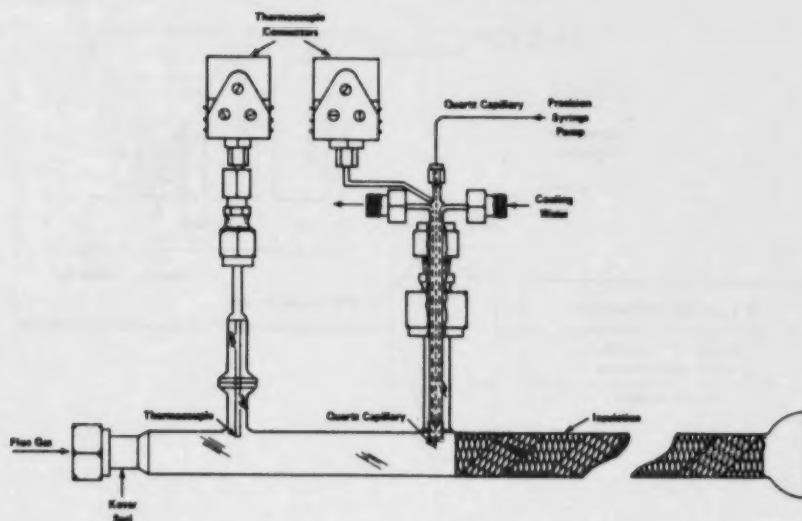


Figure 4. TCDD Spike Injection System.

externally heated to maintain the required gas stream temperatures from the point of spiking into the samplers (SASS and MM5). A summary of operational parameters for the flue gas sampling systems is shown in Table 1. For both the SASS and MM5 tests the flue gas temperature at the injection point was 260°C (500°F). The filter temperature in the SASS was held at 204°C (400°F), whereas the MM5 was held at 120°C (250°F) filter temperature. The operating upper temperature limit for the XAD-2 traps was set at 20°C (68°F). Water at ice temperature was circulated in the jacketed condensers shown for both the SASS and MM5 trains. As illustrated in Figure 2, a double condenser section was necessary to achieve 20°C in the SASS train.

Level 1 guidelines set the total dry gas volume sampled by the SASS at 30 m³. Relatively large sample volumes were taken for MM5 tests to ensure collection times similar to actual field operation of the sampling system in incinerator applications. A total of 10 tests (numbered 1 through 10) were conducted during this program. The experimental outline is shown in Table 2. The first series consisted solely of SASS equipment and Level 1 operational procedures, while the second series employed MM5 equipment. The first test (Test 1) was a blank run to identify native concentrations of 1,2,3,4-TCDD and 2,3,7,8-TCDD, produced either by the furnace, or by sample handling. Test 2 was a blank test in which a known quantity of 1,2,3,4-TCDD was injected into the sample train; however, a dry heated air stream was used as the sampled gas. Tests 3-6 employed the SASS sampling train with the flue gas and variable spike levels of 1,2,3,4-TCDD. The MM5 tests (7-10) were completed in a similar manner using hot combustion gas starting with the highest 1,2,3,4-TCDD concentration and progressing to the lowest concentration. Two sets of tests (3 and 4, 9 and 10) were run at the same concentrations to determine experimental reproducibility.

The TCDD concentrations shown in Table 2 were the targeted concentrations. Actual concentrations varied somewhat for each test. Prior to beginning each experiment all glassware was thoroughly cleaned with methylene chloride and baked in a clean oven at 400°C (752°F) for 12 hrs. The sampling equipment was then

assembled in the combustion laboratory and attached to the tube furnace. The sampling systems were leak-checked prior to commencing an experiment. Leak rates for the SASS train were typically 8.5 x 10⁻⁴ m³/min at 635 torr. To begin the experiment the gas sampling pumps were started and temperatures allowed to equilibrate. After sampling rates were set and operating temperatures reached, the precision metering pump was turned on and set at an injection rate of 0.17-0.18 mL/min. Table 3 gives a summary of actual system conditions during the spike experiments.

CHEMICAL ANALYSES

The solvents used were Distilled-in-Glass grade hexane, benzene, carbon tetrachloride, and methylene chloride (Burdick and Jackson Laboratories, Inc., Muskegon, MI). The adsorbents used (solvent-rinsed and activated immediately prior to use) were alumina and silica gel (Biorad Laboratories, Richmond, CA). The standards used were tetrachlorodibenzo-p-dioxin-¹³C₁₂ (2,3,7,8-TCDD-¹³C₁₂) (KOR Isotopes, Cambridge, MA), and 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) (Ultra Scientific, Inc., Hope, RI). All analytical glassware was washed with soap and water, rinsed with reagent grade acetone, and baked at 400°C for a minimum of 12 hours prior to use. The XAD-2 resin, precleaned grade (Supelco, Inc., Bellefonte, PA) was extracted for 24 hrs with methylene chloride and dried prior to being packed into the sampling modules. Test batches of resin were extracted and blanks checked by glass capillary GC-FID prior to use.

Sample Extraction and Cleanup

XAD-2 resin samples were Soxhlet extracted for 16 hrs with methylene chloride. The 125 g resin samples from the SASS experiments were spiked with 2 ng of internal standard (2,3,7,8-TCDD-¹³C₁₂) prior to extraction, while the 22 g resin samples from the MM5 experiments were spiked with 0.8 ng of 2,3,7,8-TCDD-¹³C₁₂. The extraction solvent volume was 1 L for the SASS samples and 200 mL for the MM5 samples.

Methylene chloride extracts were concentrated to approximately 10 mL using a Kuderna-Danish concentrator. The

TABLE 1. OPERATING PARAMETERS FOR THE SAMPLING SYSTEMS

Fuel	Natural Gas
Sampling Volumes	
SASS	30 m ³ (1060 ft ³)
Modified Method 5	6.0 m ³ (200 ft ³)
Flue Gas Sampling Rate	
SASS	0.11 m ³ /min (4 scfm)
Modified Method 5	0.02 m ³ /min (0.8 scfm)
Spike Solution Injection Rate	Approximately 0.2 mL/min
Filter Temperatures	
SASS	204°C (400°F)
Modified Method 5	120°C (250°F)
XAD-2 Resin Bed Temperatures	
SASS	<20°C (68°F)
Modified Method 5	<20°C (68°F)

TABLE 2. EXPERIMENTAL OUTLINE

Test Number	Gas	TCDD ^(a) Concentration	Sampling Apparatus	Proposed Sample
1	Flue Gas	0	SASS	Blank
2	Hot Air	1000	SASS	1,2,3,4-TCDD
3	Flue Gas	1000	SASS	1,2,3,4-TCDD
4	Flue Gas	1000	SASS	1,2,3,4-TCDD
5	Flue Gas	100	SASS	1,2,3,4-TCDD
6	Flue Gas	10	SASS	1,2,3,4-TCDD
7	Flue Gas	1000	MM5	1,2,3,4-TCDD
8	Flue Gas	100	MM5	1,2,3,4-TCDD
9	Flue Gas	10	MM5	1,2,3,4-TCDD
10	Flue Gas	10	MM5	1,2,3,4-TCDD

(a) Flue gas concentration (pg/m^3) at 20°C.

TABLE 3. SYSTEM OPERATING CONDITIONS

Test Number	1	2	3	4	5	6	7	8	9	10
Gas Temperature, °C ^(a)	260	233	263	254	257	251	258	258	256	262
Filter Temperature, °C	203	212	201	193	187	208	130	128	129	129
XAD-2 ^(b) Temperature, °C	5.00	5.00	6.10	6.67	8.33	7.22	6.67	6.28	5.44	6.11
O ₂ , percent	5.0	5.0	5.1	4.9	4.7	4.9	4.7	5.0	5.1	4.9
Sampling Rate, m ³ /min	0.113	0.112	0.112	0.114	0.116	0.117	0.021	0.021	0.021	0.021
Gas Volume ^(c) Sampled, m ³	28.7	30.2	30.6	30.2	30.7	30.7	5.50	5.54	5.69	5.53
Solvent Injection Rate, mL/min	0.18	0.17	0.17	0.17	0.17	0.18	0.17	0.17	0.18	0.17

(a) Gas temperatures measured at the point of injection.

(b) Temperatures measured at XAD-2 outlet.

(c) Dry volumes at 20°C.

extracts were further concentrated after transfer to tubes (with drawn out tips) using three 2 mL hexane rinses and carefully solvent-exchanged into 5 mL of hexane.

All extracts were cleaned up using column chromatography with a combination of silica, modified silica, and alumina. The extracts were first passed through a multilayered silica column containing silica, 44% sulfuric acid on silica, and 33% 1 molar sodium hydroxide on silica. The acid, neutral, and basic silicas were placed in layers. The column was pre-rinsed with hexane, and extract was added, followed by column elution with 1:1 hexane/benzene. The total eluent was collected, concentrated, and solvent-exchanged into 5 mL of hexane. The extract was then added to a column containing 5 g of precleaned and activated alumina. This column was sequentially eluted with hexane, hexane/carbon tetrachloride (1:1), and hexane/methylene chloride (1:1). The hexane/methylene chloride fraction was collected and gently taken nearly to dryness. The extract was dissolved in 20 mL of n-decane and stored at 0°C until analyzed. The sequential cleanup procedure is shown in Figure 5.

HRGC/HRMS Procedure

The extracts were analyzed by combined HRGC/HRMS. A VG Model 7070H HRMS directly coupled to a Carlo Erba Model 4160 GC was used for the analyses. Data were acquired by a VG Model 2035 foreground/background data system. The MS was operated in the electron ionization mode at a resolution of 10,000-12,000 (M/ΔM, 10% valley).

Five ion masses were monitored using the VG Digital MID unit which included a prototype 20-bit digital-to-analog converter for accelerating voltage and electrostatic analyzer voltage control. The monitored masses were: 319.8965 and 321.8936, the most intense peaks in the molecular ion cluster of native TCDDs; along with 331.9368 and 333.9338, the most intense peaks in the molecular ion cluster of the internal standard. A peak for perfluorokerosene, 318.9792, was used as a lock mass by the data system to control mass focus.

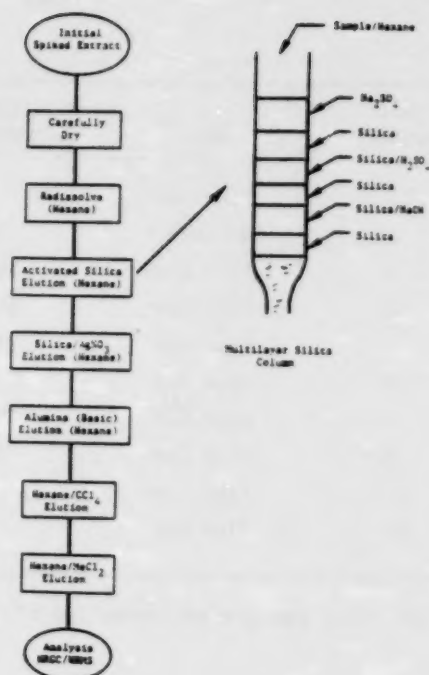


Figure 5. Schematic Diagram of the Sequential TCDD Cleanup Procedure.

The chromatographic column was a 30 m, DB-5 coated, fused silica capillary interfaced directly into the ion source. Helium carrier gas was used at a flow velocity of 21 cm/sec. Sample injection was made at 150°C with a 3-min hold time followed by a linear temperature increase of 30°C/min to 280°C. The final temperature was maintained for 12 min. Under these conditions 2,3,7,8-TCDD-¹³C₁₂ and 1,2,3,4-TCDD had retention times of approximately 13 min each. Recent papers by Harless *et al.* (6-7) demonstrated the sensitivity and selectivity obtainable by the combination of HRGC and HRMS to accurately measure low levels of TCDD isomers.

Calibration Procedures

Calibration was based on comparing responses from known amounts of 1,2,3,4-TCDD (the analyte of interest) with a

known amount of 2,3,7,8-TCDD- $^{13}\text{C}_{12}$ (the internal standard).

The 1,2,3,4-TCDD standard was the same as that injected in the hot gas stream. All solutions of this material were based on the same gravimetrically prepared stock solution. The internal standard material, 2,3,7,8-TCDD- $^{13}\text{C}_{12}$, was obtained in solution. However, its concentration was checked with gravimetrically prepared standards of native 2,3,7,8-TCDD from four sources: EPA (R. Harless, EPA/RTP), University of Nebraska (Lincoln), McMaster University (Toronto, Canada), and Monsanto Research Corporation (Dayton, OH).

The instrumental response ratio between the analyte material and the internal standard was obtained by analysis of a portion of the flue gas injection solution that was spiked with the internal standard solution. Since the concentration of analyte was based on comparing its response to a labeled isomer, calibration was carried out with every analysis run.

Data Reduction, Validation, and Reporting

Both stack gas spikes and internal standards were used in this study, and recoveries are reported for each. It is important to note the difference between them and how they were used. The spike was added to the stack gas slipstream before the sampling train. This value was used to calculate the collection efficiency of the sampling system. The internal standard was added to the resin after sampling was completed. Its purpose was to determine the extraction, cleanup, and analytical recovery. The collection efficiency was corrected for the recovery of the internal standard.

The amount of recovered 1,2,3,4-TCDD was calculated by the relationship:

$$\text{ng 1,2,3,4-TCDD} = \frac{\text{Area m/e 322 (1,2,3,4-TCDD)}}{\text{Area m/e 334 (2,3,7,8-TCDD-}^{13}\text{C}_{12})} \times \frac{2.5 \text{ ng}^*}{\text{Fraction of Sample Extracted}}$$

* = ng of 1,2,3,4-TCDD added.

Data validity was ensured through application of the following procedures:

- Daily tuning the mass spectrometer for resolution and area response.
- In every run, the internal standard must be from 1/2 to 2 times the expected response (the response observed in a test mix of known concentration).

RESULTS AND DISCUSSION

The analytical determinations in Test 1 (system blank using flue gas) and Test 2 (system spike using heated air) were completed before the actual SASS/MM5 challenge tests were performed. In Test 1, the system blank, no detectable 1,2,3,4-TCDD or 2,3,7,8-TCDD was found at the minimum detectable amount (1 pg) injected. For Test 2, spiked hot air, subsamples were analyzed representing several regions of the SASS train, regions where TCDDs might condense or accumulate. The results of those analyses are shown in Table 4 where recoveries are shown to total about 94%. An instrument fault occurred in the computer system while computing the XAD-2 extract data, and the quantification of the reported 70% resin trap recovery could not be verified by exact area computation. This value is approximate but represented the major portion of the 1,2,3,4-TCDD and showed a high recovery overall for the system spike.

CHOICE OF SPIKE LEVELS FOR TESTS 3-10

A series of technical review meetings included consideration of proposed spike levels in relation to source discharge levels and analytical sensitivity. These data have received much attention, and to date no definitive study of incinerator discharge levels for TCDDs has been performed. The proposed analytical system is capable of subpicogram sensitivity for individual TCDD isomers, and spiking levels of 1000, 100, and 10 pg/m³ were proposed. Based on typical collection volumes for the SASS and MM5 trains, the total weight of 1,2,3,4-TCDD spiked ranged from 60 pg to 30 ng as shown in Table 5. A syringe volume of 50 mL was used with the

TABLE 4. EPA INCINERATION SIMULATION RECOVERIES--TEST 2

Amount of 1,2,3,4-TCDD Recovered (pg)	Percent Recovery (%)	SASS Test Section
50	0.2	Injector liner
ND ^(a)	--	Heated flue
260	1.1	Filter
4,800	23	Transfer line to XAD-2
17,500	70 ^(b)	XAD-2 resin
Total Recovery	~94	

(a) Not detected.

(b) Approximate.

TABLE 5. TCDD LEVELS ADDED TO HOT STACK GAS

Spike Level	TCDD Concentration (pg/m ³)	Total TCDD SASS (30 m ³)	Total TCDD MM5 (6 m ³)
High	1000	30 ng	6 ng
Medium	100	3 ng	600 pg
Low	10	300 pg	60 pg

precision metering pump to deliver the dioxin spike solution; and since gas collection rates of 6.8 m³/hr for the SASS train and 1.3 m³/hr for the MM5 train were used in sample collection, 1,2,3,4-TCDD spike solutions of 1-600 ng/L, liquid concentration, were required. This corresponds to an approximate delivery rate of 0.17-0.18 mL/min. This rate was high enough to flush the transfer probe and prevent condensation in the capillary.

The choice of an optimum solvent was based on delivery rate, viscosity, solubility of 1,2,3,4-TCDD, boiling point, XAD-2 retention, and demonstrated purity. The solvent system developed was acetone with 0.5% (v/v) decane as a "keeper." Decane also served to flush residual 1,2,3,4-TCDD from the transfer probe. The acetone acted as a volatile carrier for the 1,2,3,4-TCDD and was not retained in the XAD-2 resin bed.

RECOVERY STUDIES--TESTS 3-10.

Tests 3-10 were designed to challenge both the SASS and MM5 sampling systems at gas-phase concentrations expected to cover a range from high levels to the minimum levels detectable by available analytical methodology. Results of this series of experiments are given in Table 6 which includes the dry air spike experiment (Test 2).

These data show good internal consistency and high recoveries for each experiment, except Test 10, where a 229% recovery was observed. No experimental evidence exists to explain this unusual result. On balance the data show that both the SASS and MM5 trains work well with the isotope dilution HRGC/HRMS analytical technique to recover TCDDs as modeled by recovery of 1,2,3,4-TCDD from hot flue gas streams.

It is noted that the distribution of 1,2,3,4-TCDD among the heated and cooled sections of the SASS and MM5 trains may vary as a function of the combustion source tested. Dioxins may have a high adsorptive affinity for the particulate matter found in some sources. It is interesting to note in Test 2, the dry air experiment, that a major portion of the spiked 1,2,3,4-TCDD was found in the cold regions of transfer tubing leading

into the resin trap (23% in transfer line). To investigate the effect of moisture condensation on the operation of the sampling systems two separate investigations were performed: for the SASS samples (Tests 3-6), the heated "front half" of the train (probe rinse, filter housing, filter, and heated transfer line wash) was analyzed separately from the cooled "back half" of the train (cooled transfer line washes, resin bed, and condensate). In all four experiments, less than 1% of the spiked 1,2,3,4-TCDD was found in the heated "front half" of the SASS train. A second series of experiments were performed to determine the possibility of TCDD breakthrough from the resin trap. For this purpose the condensates from Tests 3-6, the SASS challenge tests, were analyzed separately to determine if any of the spiked 1,2,3,4-TCDD was carried through the resin bed with condensed water. After extraction and concentration, no measurable levels of 1,2,3,4-TCDD could be detected in the condensates from Tests 3-6, thus demonstrating the effectiveness of XAD-2 to trap TCDDs even in moisture-laden combustion gas streams.

SUMMARY

This study demonstrated a high dioxin collection efficiency using two stack sampling techniques, the SASS and MM5 trains. In eight combustion tests, a system blank, and a spiking experiment with hot dry air, recoveries of 1,2,3,4-TCDD were quantitative except in one instance. The spiking device developed in this study incorporated several features that make it useful for spiking a broad range of test compounds directly into hot flue gas streams in order to generate a stream of known concentration. Such a spiking device is necessary to evaluate the performance of candidate sampling and analysis procedures for stationary source testing.

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TABLE 6. 1,2,3,4-TCDD RECOVERIES FROM TESTS 2-10

Test Number	Sampler System	Liquid Spike Volume (mL)	1,2,3,4-TCDD			Percent Recovery
			Liquid Concentration (pg/mL)	Expected Concentration (ng)	Calculated Concentration (ng)	
2 (Dry Air)	SASS	49	500	24	23	-94
3	SASS	51	500	25	18	73
4	SASS	42	50	21	17	83
5	SASS	50	5	2.5	2.9	117
6	SASS	51	5	0.25	0.28	113
7	MM5	47	15	7.1	8.0	113
8	MM5	47	12	0.56	0.57	101
9	MM5	49	8	0.39	0.47	120
10	MM5	47	8	0.38	0.87	229

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DISCLAIMER

Mention of trade names or products does not constitute endorsement or recommendation for use by the United States Environmental Protection Agency.

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STACK SAMPLING AND ANALYSIS OF FORMALDEHYDE

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ABSTRACT

A collection medium of potential use for the determination of formaldehyde in stationary combustion research and development projects was evaluated in a laboratory test atmosphere. The medium consists of a porous polymer sorbent, i.e., XAD-2®, coated with 5% by weight of 2,4-dinitrophenylhydrazine hydrochloride (2,4-DNPH·HCl). Formaldehyde is retained on this medium by adsorption and formation of the 2,4-dinitrophenylhydrazone derivative. Analysis was conducted by reverse phase HPLC with an acetonitrile/water eluant.

The laboratory evaluation consisted of:

- Sampling/Analysis of a formaldehyde test atmosphere
- Sampling/Analysis of a simulated stack matrix
- Analysis of spiked samples
- Evaluation of storage stability
- Independent analysis.

The precision (relative standard deviation) associated with the sampling/analysis of the formaldehyde atmosphere with the test medium was observed to be 7.1%. The measured formaldehyde concentration was within $\pm 1\%$ of the "true" concentration as determined by the chromotropic acid method.

Samples collected from the stack matrix were spiked with formaldehyde. Observed recovery was 107%. Samples stored for seven days showed an increased apparent formaldehyde content of about 17%.

INTRODUCTION

The possible presence of designated high-probability carcinogens (HPCs) in the effluent of a stationary combustion source is dependent on the nature of the fuel or other feedstock and on the combustion efficiency. Complete combustion of materials in these sources requires sufficient air (oxygen), turbulent mixing, and a high temperature maintained over a long period of time. Non-optimum combustion conditions, such as inadequate amounts of air within the combustion zone or within localized subzones, will result in unburned or only partially burned organic material. The vaporous material can include acids, aldehydes, and

other more complex organic species. These species are of particular concern during the evaluation of combustion modification techniques since care must be taken that such modifications do not lead to additional environmental problems.

In a literature survey for the EPA(1) which focused on sampling/analysis (S/A) of the 21 designated HPCs, formaldehyde was among a few HPCs selected as a "special needs" group. These "special needs" compounds were categorized as requiring immediate sampling and analysis method attention before being selected as candidates for

combustion-source studies. The EPA survey report concluded that the previously recommended S/A procedure for formaldehyde (i.e., using 3-methyl-2-benzothiazolone hydrazone [MBTH]) should be replaced since sulfur dioxide (SO_2), which is found in stationary combustion source effluent, negatively interferes with the aldehydes measurements in that method (2). The report suggested an alternative approach involving the formation of the 2,4-dinitrophenylhydrazone derivative of the aldehyde. Two methods based on this recommendation are currently in use, but have not been evaluated for use in stack gas analysis. The first, a liquid impinger method, has been routinely used in the past for diesel exhaust analysis of carbonyls (2,3). More recently a second method using 2,4-dinitrophenylhydrazine hydrochloride coated XAD-2® (termed a chemosorbent) in a solid sorbent tube has been developed (4,5). Because of its ease of operation, the chemosorbent method was selected for evaluation.

In evaluating the candidate S/A method for collection of formaldehyde in a simulated stationary combustion source effluent, several points were considered. Of prime consideration was the accuracy of the test method versus that of an accepted independent method (chromotropic acid) (6). Another concern was the comparison of the results from the simulated stack gas analyses versus the data from clean air background analyses, indicating possible interferences or chemical reactivity. Lastly, the stability of stored samples was explored. In short, the test method was expected to be able to provide a viable collection medium for formaldehyde in the simulated combustion matrix in terms of ease of operation, precision and accuracy.

EXPERIMENTAL

An atmosphere simulating a stationary combustion source effluent was generated in the laboratory. The atmosphere consisted of a mixture of gases at concentrations which might be expected in the stack gas. The gas matrix generated was 10% CO_2 , 1000 ppm NO_x , 100 ppm SO_x with 68% relative humidity (RH). The formaldehyde level produced was approximately 5 ppm by volume.

Simulation of the stack gas was achieved by addition of component gases into a vapor dilution system (Figure 1). The system had a designed air flow of 100 L/min at the

inlet. The air was pretreated to remove any particulate matter, organics or water. The standardized component gases were then individually added into the dilution system.

Formaldehyde was added first to the clean air. A 3.3% formalin solution in water was added to the system at the rate of .041 mL/min. Theoretically, this would have produced a formaldehyde atmosphere of 14 $\mu\text{g/L}$. However, due to the polymerization of formaldehyde to paraformaldehyde in the system, an atmosphere of approximately 40% of the theoretical concentration, or about 5.6 μg formaldehyde/L air, was generated.

Further downstream the background gases were introduced to simulate a stationary combustion source. Nitric oxide (NO) was delivered into the system as a 10% mixture in nitrogen at 10 mL/min. Sulfur dioxide (SO_2) and carbon dioxide (CO_2) were added as pure gases at the rate of 100 mL/min and 11 L/min, respectively. The total dry gas through the system, therefore, was approximately 111 L/min. The water was added at the rate of 1.4 mL/min and vaporized into the system (Figure 2) producing .10 g $\text{H}_2\text{O/g}$ dry gas. At an ambient temperature of 20°C this was equivalent to a RH of approximately 68%.

Replicate samples were collected for analysis of formaldehyde by both the test and independent methods simultaneously. In the chromotropic acid determination method, collection was made in a 1% sodium bisulfite solution in midget bubbler pairs connected in series. Each impinger contained 15 mL of the bisulfite solution. The DNPH chemosorbent method collection was accomplished through a 5% coating of 2,4-dinitrophenylhydrazine hydrochloride on XAD-2® packed in glass tubes.

The chemosorbent was prepared in the laboratory by coating the DNPH·HCl on to the resin, as follows:

- The DNPH·HCl was made by dissolving 2,4-dinitrophenylhydrazine in hot 4N HCl.
- The hydrochloride produced was crystallized by cooling and recrystallized again from fresh 4N HCl.
- The hydrochloride was then dissolved in a 9:1 mixture of ethanol:HCl (conc) to produce a 5% coating on the XAD-2®.
- The solution was placed in a rotary

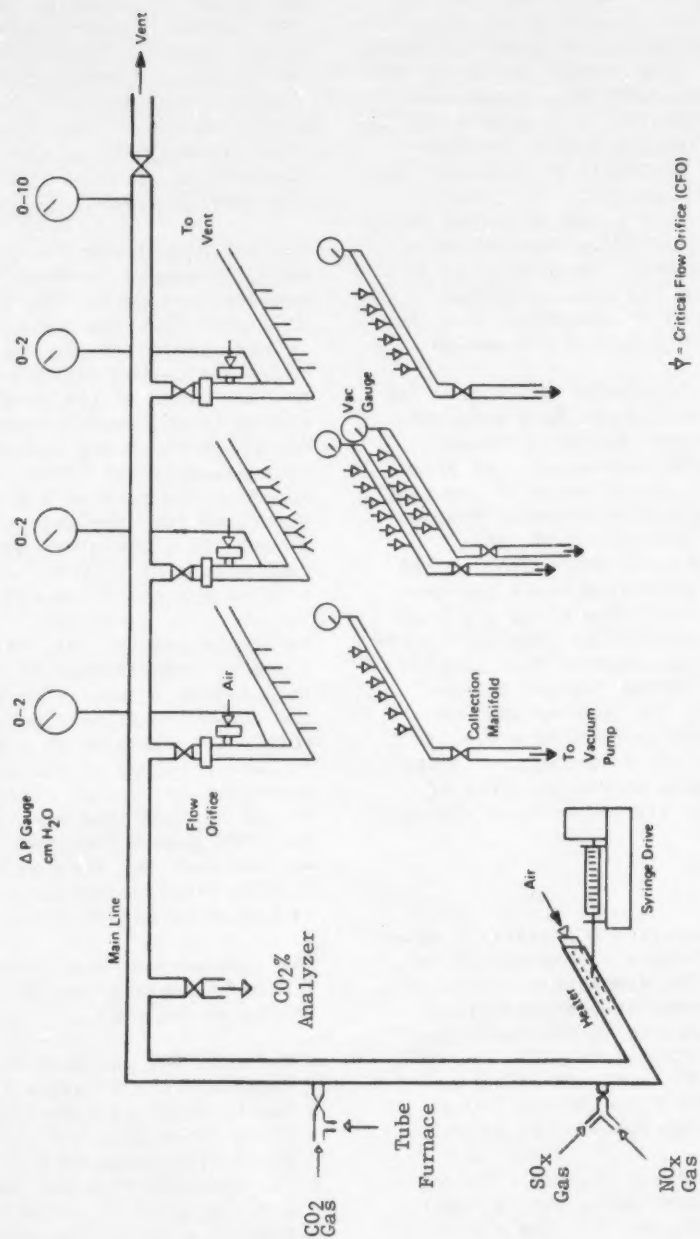


Figure 1 Apparatus for Vapor Generation/Dilution/Sampling System

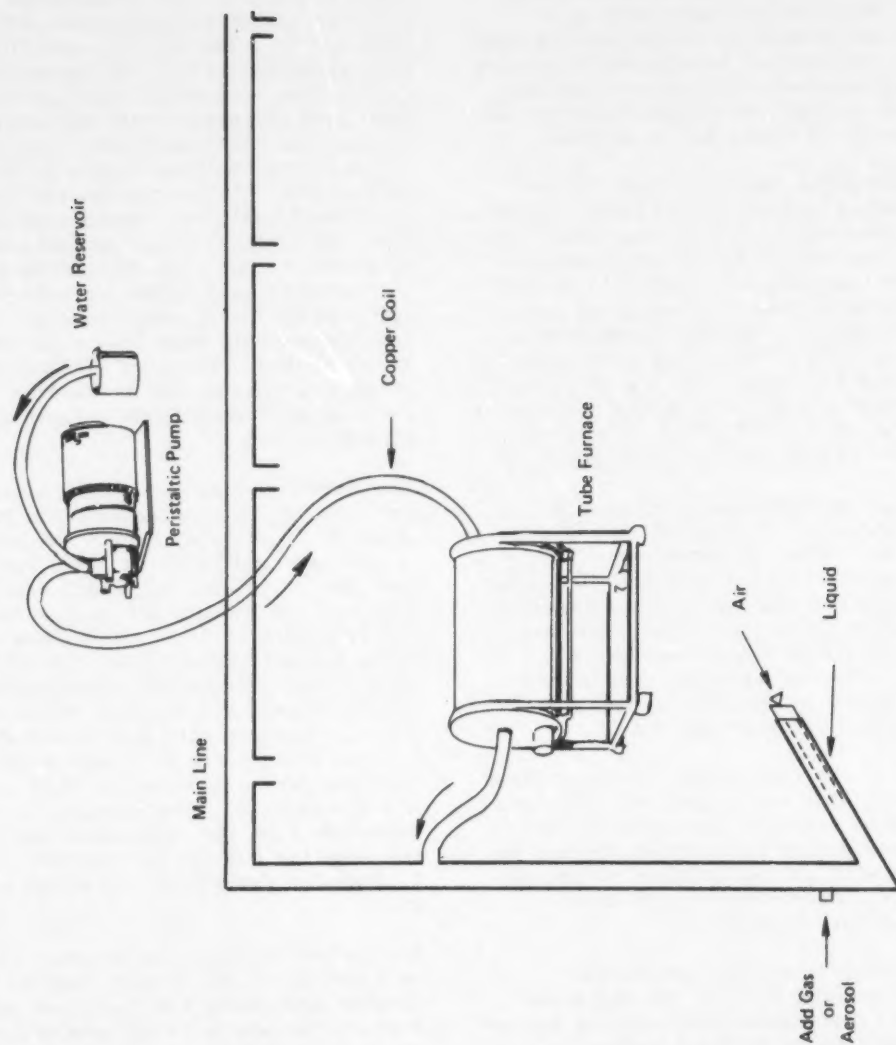


Figure 2 Apparatus for Generation of High Humidity Atmospheres

evaporator with clean XAD-2® and the solvent removed.

- The dry chemosorbent (ca 200 mg/tube) was then packed into 10 cm x 6 mm OD (1 mm wall) glass tubes, with glass wool plugs.

The flow through each of the sample ports was controlled by a critical flow orifice, calibrated with a typical sampling device in line. All orifices were used on a single vacuum system to ensure simultaneous sampling. Collection through the impingers was at approximately 1 L/min for one hour. Collection through the chemosorbent was at approximately .2 L/min for 20 minutes.

Immediately after sampling, half of the samples were prepared for analysis, while the rest were sealed for storage stability testing. The sodium bisulfite collection pairs were combined and diluted to 50 mL, from which an aliquot was taken and analyzed according to the APHA chromotropic acid method (#116). The chemosorbent samples were removed from their tubes and desorbed with acetonitrile in small vials and analyzed directly by HPLC using an acetonitrile/water eluant and 365 nm UV detector.

Accuracy of the methods was checked by standard addition. One-third of the samples for the stored chemosorbent set were spiked with an amount of a dilute formalin solution equal to the amount expected from the generator collection. This standard addition method provided a measure of quality control and absolute accuracy of the test method by confirming compound identification and recovery data.

Precision of the test method was determined by agreement of the replicate formaldehyde concentration results. Accuracy of the chemosorbent method was further checked by comparison with the independent reference method, i.e., chromotropic acid determination of formaldehyde.

Storage stability of the samples was checked by sealing half of the collected samples in their respective sampling devices and setting them aside for a period of seven (7) days in the dark at ambient conditions.

RESULTS

The evaluation of the DNPH/XAD-2® method consisted of two independent studies. The chemosorbent was first evaluated in a clean

air environment, i.e., no interfering background gases, at low humidity (<5% RH). Two atmospheres of formaldehyde were generated under identical conditions and the results pooled (see Table 1). The results show excellent agreement between the DNPH·HCl coated XAD-2® chemosorbent and the chromotropic acid reference methods. An atmosphere containing the formaldehyde at a slightly higher concentration with 10% CO₂, 1000 ppm NO_x, 100 ppm SO_x, and 70% RH was then produced. Again, two separate collections were made. Half of the samples from each collection were set aside for storage stability analysis. The remaining samples were analyzed within 24 hours of collection. The pooled results from the "next day" analyses (short-term storage), shown in Table 2, again indicate excellent agreement between the chemosorbent and the chromotropic acid reference methods, 6.17 µg/L and 6.12 µg/L respectively. These results indicate that the acidic nature of an unscrubbed combustion effluent should produce no bias on the collection and analysis of formaldehyde using the chemosorbent method.

The stored samples (long-term storage) indicate the same agreement. As shown in Table 3, the samples stored for seven days at ambient conditions in their sealed sampling containers had concentrations of 7.45 µg/L by the chromotropic acid method and 7.20 µg/L by the chemosorbent method. These results represent a statistically significant increase in formaldehyde concentration, for the four pairs of chromotropic acid results and nearly the same for the seven pairs of chemosorbent results (one outlier pair from the eight analyzed was disregarded). Entrainment of paraformaldehyde from the generation system into the sampling devices may account for the increased formaldehyde concentration over time.

The evaluation of spike recovery performed on a number of the storage samples shows results confirming the excellent agreement. Four of the sample tubes were spiked with 20 µg of formaldehyde in solution, prior to the collection on the generator system. Recovery data were calculated assuming a theoretical collection based on the mean measured formaldehyde level and the collected volume of vapor. The percent recovery was found by subtracting the amount of formaldehyde expected from the generating system alone from that actually recovered. Using this method, a mean recovery of 107%

TABLE 1: FORMALDEHYDE COLLECTION - "CLEAN AIR" RESULTS (Combined from two sample runs)

Sample No.	Total CH ₂ O (μ g)	Chromotropic Acid		CH ₂ O Conc (μ g/L)	
		Volume Sampled (L)			
1	80.88	15.63	5.17	Run 1	
2	77.00	15.57	4.95		
3	87.63	18.82	5.54		
4	92.00	15.30	6.01		
5	65.64	15.63	4.20	Run 2	
6	72.43	15.57	4.65		
7	29.40	15.82	1.86*		
8	66.06	15.30	4.32		
Mean					4.97
Std. Dev.					.654
C.V.					.131

Sample No.	Total CH ₂ O (μ g)	DNPH/XAD-2 [®] (Chemosorbent)		CH ₂ O Conc (μ g)	
		Volume Sampled (L)			
1	53.72	10.74	5.00	Run 1	
2	49.34	10.58	4.66		
3	51.20	11.04	4.63		
4	53.26	11.46	4.65		
5	48.71	10.55	4.62	Run 2	
6	57.36	10.74	5.34		
7	58.79	10.58	5.55		
8	53.76	11.04	4.87		
9	61.99	11.46	5.41		
10	53.22	10.55	5.05		
Mean					4.98
Std. Dev.					.355
C.V.					.071

Source: Results in above table obtained from a report prepared for U.S. Bureau of Mines
 *Values omitted from data summary.

Note: All samples have been corrected for blanks which accounted for less than 3% in each of the samples.

C.V. Coefficient of Variation (= Relative Standard Deviation)

TABLE 2: FORMALDEHYDE COLLECTION IN SIMULATED STACK GAS - "NEXT DAY" ANALYSES

	<u>Chromotropic Acid</u>		
<u>Sample No.</u>	<u>Total CH₂O</u> <u>(μg)</u>	<u>Volume Sampled</u> <u>(L)</u>	<u>CH₂O Conc</u> <u>(μg)</u>
1	349	59.5	5.87
2	441	76.5	5.76
3	410	59.5	6.89
4	455	76.5	5.95
Mean			6.12
Std. Dev.			.521
C.V.			.083

TABLE 2 (Continued)

Sample No.	Total CH ₂ O	DNPH/XAD-2® (Chemosorbent)		CH ₂ O Conc
	(μ g)	Volume Sampled		
		(L)		(μ g/L)
1	16.4	2.66		6.17
2	19.7	3.75		5.26
3	27.9	3.73		7.47
4	17.4	2.45		7.08
5	3.32	2.66		1.25*
6	16.9	3.75		4.50
7	23.9	3.73		6.39
8	15.5	2.45		6.32
Mean				6.17
Std. Dev.				1.02
C.V.				.165

*Values omitted from data summary.

Note: All samples have been corrected for blanks which accounted for less than 2% in each of the samples.

TABLE 3. FORMALDEHYDE COLLECTION IN SIMULATED STACK GAS - STORAGE STABILITY DATA

<u>Sample No.</u>	<u>Total CH₂O</u> <u>(μg)</u>	<u>Chromotropic Acid</u>		<u>CH₂O Conc</u> <u>(μg)</u>
		<u>Volume Sampled</u> <u>(L)</u>		
1	108	15.72		6.87
2	353	54.72		6.45
3	141	15.72		8.92
4	411	54.72		7.51
Mean				7.45
Std. Dev.				1.10
C.V.				.148

Sample No.	Total CH ₂ O	DNPH/XAD-2® (Chemosorbent)		CH ₂ O Conc
	(µg)	Volume Sampled		(µg/L)
1	30.0	3.69		8.11
2	28.6	3.68		7.78
3	21.9	2.54		8.62
4	6.57	1.12		5.87
5	26.8	3.69		7.27
6	26.3	3.68		7.14
7	19.2	2.54		7.56
8	5.90	1.12		5.27
Mean				7.20
Std. Dev				1.12
C.V.				.156

Note: All samples have been corrected for blanks which accounted for less than 1% in each of the samples.

was determined (see Table 4). Allowing for variation in the actual collections on the vapor generator, these results indicate a probable recovery of 100%.

CONCLUSIONS

The DNPH/XAD-2® chemisorbent appears to be a viable method for the sampling and analysis of formaldehyde in incineration or combustion source environments. The chemisorbent is relatively simple to prepare and remains stable for several months if stored in the dark. The sorbent tube has proven to be a very convenient method to use in the field in terms of ease of handling and in shipping. The chemisorbent has the added feature of producing a slight color change from yellow/brown to yellow as the hydrazone is formed, allowing the user to know if breakthrough is imminent. The tube is easily desorbed for analysis, and the results are specific for formaldehyde. Overall, the method appears to be a prime candidate for formaldehyde S/A, and could possibly, be extended to provided specific methods for other carbonyls. Additional testing may be required for applicability

at higher stack temperatures.

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DISCLAIMER

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TABLE 4: FORMALDEHYDE COLLECTION IN SIMULATED GAS - SPIKE RECOVERY DATA (7.2 µg/L Atmosphere)

Sample No.	Volume Sampled	Expected CH ₂ O	Recovered CH ₂ O	Differences Due to Spike	Spike CH ₂ O	Percentage Recovered
	(L)	(µg)	(µg)	(µg)	(µg)	(%)
1	3.47	25.0	44.4	19.4	20	97.0
2	5.29	38.1	62.2	24.1	20	120
3	3.47	25.0	44.5	19.5	20	97.5
4	5.29	38.1	60.9	22.8	20	114
Mean						107
Std. Dev.						11.7
C.V.						.109

Note: All samples have been corrected for blanks which accounted for less than 2% in each of the samples.

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FACTORS AFFECTING THE GAS-PHASE
THERMAL DECOMPOSITION OF
CHLORINATED AROMATIC HYDROCARBONS

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ABSTRACT

In this presentation, we report the results of laboratory studies concerning the high-temperature gas-phase thermal decomposition of seven different chlorinated benzenes. The generally observed trend is toward increasing thermal stability with increased chlorine substitution. The relationship of thermal decomposition to time and temperature can be adequately described by first order kinetics and application of the Arrhenius equation. Studies of the effect of oxygen concentration on the thermal decomposition of hexachlorobenzene and pentachlorobenzene suggest that the susceptibility to oxygen attack is reduced with increased chlorine substitution. Data also suggest that the decomposition mechanism changes with temperature.

INTRODUCTION

Regulating the disposal of hazardous waste as promulgated by the Resource Conservation and Recovery Act (RCRA) of 1976 has made some traditional methods of disposal, such as impounding and landfilling, less desirable and consequently, incineration

much more desirable. Under the current interim final rule (1) on incineration, the incinerator operator must show that the facility can destroy those waste constituents most difficult to incinerate. In theory the permit writer will select compounds within the mixture that are of sufficient toxicity, concentration,

and thermal stability so as to be designated as principal organic hazardous constituents (POHCs). It must then be shown, possibly by trial burn, that the designated POHCs can be destroyed by the particular incineration system to a destruction and removal efficiency (DRE) of 99.99%. Furthermore, the specific operating conditions must be established under which the 99.99% DRE is achieved.

A universal ranking procedure which readily allows determination of thermal stability and designation of POHCs is of interest to everyone, but primarily to the permit writer. The incinerator operator is by necessity concerned with both economical operation and the determination of the optimum waste disposal conditions. It is generally acknowledged that incineration is a complex process and our present knowledge does not permit the designation of POHCs and overall operating conditions without some uncertainty.

One approach to establishing optimum incineration conditions is to perform the necessary determinations by trial and error using the actual incineration system; however, due to the difficulty of controlling all of the parameters affecting full-scale incineration, this approach can be inefficient, incorrect, and time consuming. Extrapolation of data from one facility to another is very difficult (2) due to differences in wastes, basic design characteristics, and the inability to develop simple physical models for complex systems.

An alternative approach is to generate data in the laboratory using well characterized and controlled conditions. The challenge in this approach is to determine which incineration variables are most significant with respect to destruction efficiency (DE) and design suitable laboratory experiments which permit evaluation of these variables in a manner that is amenable to eventual scale up conditions.

Since the nominal conditions within the flame zones of large field-scale incinerators are usually sufficient to decompose any gas-phase waste components, our approach has been to address the 'exceptional' molecules which escape this highly reactive environment. Although temperatures are much higher in the flame than non-flame region of the incinerator, molecules will experience a much greater residence time in the non-flame region. (It is this region, i.e., the non-flame region of the afterburner, that provides the final thermal decomposition environment which significantly contributes to the attainment of an overall system DRE of 99.99%.)

In this presentation we address a class of compounds known both for their toxicity and thermal stability, the chlorinated hydrocarbons (CHCs). We report the results of our studies which were designed to gain insight into the factors which control the non-flame thermal decomposition of these compounds. In this work we have attempted to separate the chemical parameters from the physical parameters. We then

studied the effect of the chemical parameters on thermal stability of the test compounds. Specifically, we have addressed the effect of reaction atmosphere (oxygen concentration), mean residence time, and temperature on various chlorinated benzenes. A simple mechanistic model is proposed to account for the observed form of the thermal decomposition profiles.

Experimental

The affect of mean residence time and temperature on the thermal decomposition of chlorinated benzenes was determined on the thermal decomposition unit-gas chromatographic (TDU-GC) system which was designed and built with funding provided by the US-EPA (Cooperative Agreement No. CR-807815-01-0). A block diagram of the TDU-GC is shown in Figure 1. The data pertaining to the effect of oxygen concentration on thermal decomposition behavior was obtained using the thermal decomposition analytical system (TDAS), also designed and built with funding provided by the US-EPA (Grant No. R805117-01-0). These units are quite similar in design and operation and data compares very favorably between the two systems. Their major difference is that the TDAS utilizes an LKB 2091 GC/MS for data acquisition. (3) Kinetic data from the TDAS was obtained using the GC in combination with the total ion current (TIC) detector of the mass spectrometer.

Both thermal reactor assemblies are constructed of 1 mm nominal I.D. fused quartz tubing in a race track configuration

(3.5 cycles, 1 meter in length). This quartz tubular reactor construction was chosen to minimize the possibility of wall reactions while simultaneously providing a very narrow residence time distribution and a square-wave high-temperature exposure profile. (4)

High vapor pressure liquid phase samples were prepared at concentrations of approximately 10 ppm in air. (Precise quantitation is not required since data reduction employs a difference method involving the comparison of the partially decomposed sample peak size with a non-decomposed quantitation peak.) These samples were slowly injected into a flowing air carrier stream for transport through the reactor. Low vapor pressure liquid phase samples were injected onto quartz wool in a temperature programmable insertion chamber. The temperature was then increased at a rate of 12°C/min. from 0° to 250°C such that the sample was slowly volatilized for transport. Solid phase samples tested using the TDU-GC were dissolved in cyclohexane and then injected into the insertion chamber which was subsequently heated at a programmed rate. Solid phase samples that were tested using the TDAS were prepared in solution and then deposited on a glass probe whereupon the solvent was evaporated. The probe was then placed into the insertion chamber of the TDAS and heated at a programmed rate. This process, which involves a random entry-controlled thermal exposure (RE-CTE) of sample molecules, is described more thoroughly in a previous paper. (3) This mass

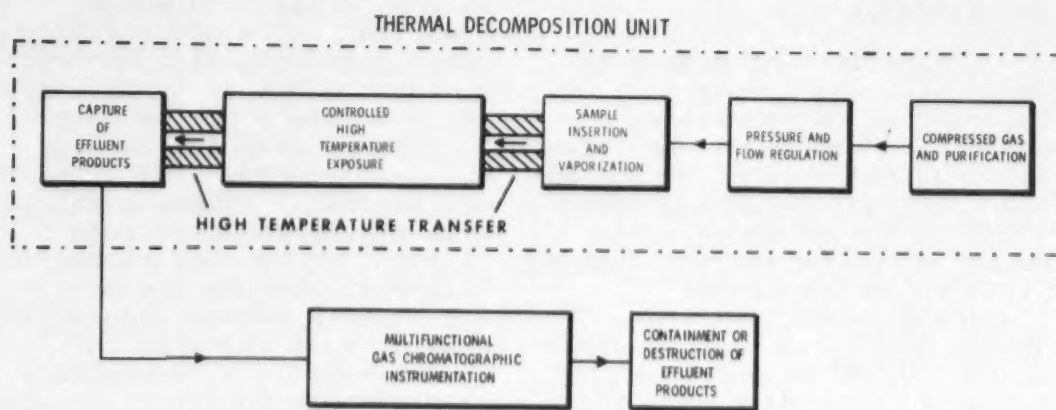


Figure 1. Block Diagram of the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) System.

transport procedure is designed to insure that the sample concentration is very dilute and in an oxygen rich environment.

Gases used in this study were purchased from Air Products, Inc. and contained less than 2 ppm total hydrocarbons. All gases were passed through a molecular sieve trap before introduction into the instrumentation systems.

Results

A homologous series of six chlorine substituted benzenes were examined to determine their thermal stability in an oxidative environment. Figure 2 depicts the thermal decomposition profiles at a mean residence time of two seconds, $t_r = 2.0$ seconds, for each of the six chlorinated benzenes studied. From these plots one can ascertain that each of the compounds is very stable with little decomposition occurring at exposure temperatures up to about 550-650°C. Once the decomposition begins, it reaches the 99.99% DE level with a further temperature increase of approximately 200°C. Table 1 presents the temperatures corresponding to the onset of thermal decomposition and the extrapolated temperatures necessary for 99.99% DE.

Data have also been obtained at $t_r = 1.0, 4.0,$ and 6.0 seconds. The family of decomposition profiles at different residence times for hexachlorobenzene (HCBz) is depicted in Figure 3. It is evident from this plot that increasing the HCBz residence time in the reactor reduces

the temperature required for a given destruction efficiency.

First order kinetic rate expressions have been found to adequately describe the time versus temperature relationship for such thermal decomposition data by applying the Arrhenius equation to the temperature dependence of the first order rate constant (5,6). However, previously obtained data (7) for 2,2',4',5,5'-pentachlorobiphenyl (2,2',4',5,5'-PCB) clearly indicated a pronounced dependence of the thermal decomposition behavior on the oxygen concentration. Specifically, the disappearance of the PCB was found to be first order in oxygen (5). This behavior indicates that the observed first order kinetics is actually a more complex phenomenon involving reaction with oxygen, possibly as the rate controlling step in the thermal decomposition. The disappearance kinetics then, are actually pseudo first order in the concentration of the parent because of the great excess of oxygen concentration over that of the test sample.

Figures 4 and 5 depict the thermal decomposition profiles for hexachlorobenzene and pentachlorobenzene at $t_r = 2.0$ seconds for various concentrations of oxygen in nitrogen from 2.5% to 70%. Over this range, it is apparent that increasing the oxygen concentration promotes the decomposition of the parent compound. However, the effect is more dramatic for pentachlorobenzene than hexachlorobenzene. In conjunction with previous observations with the

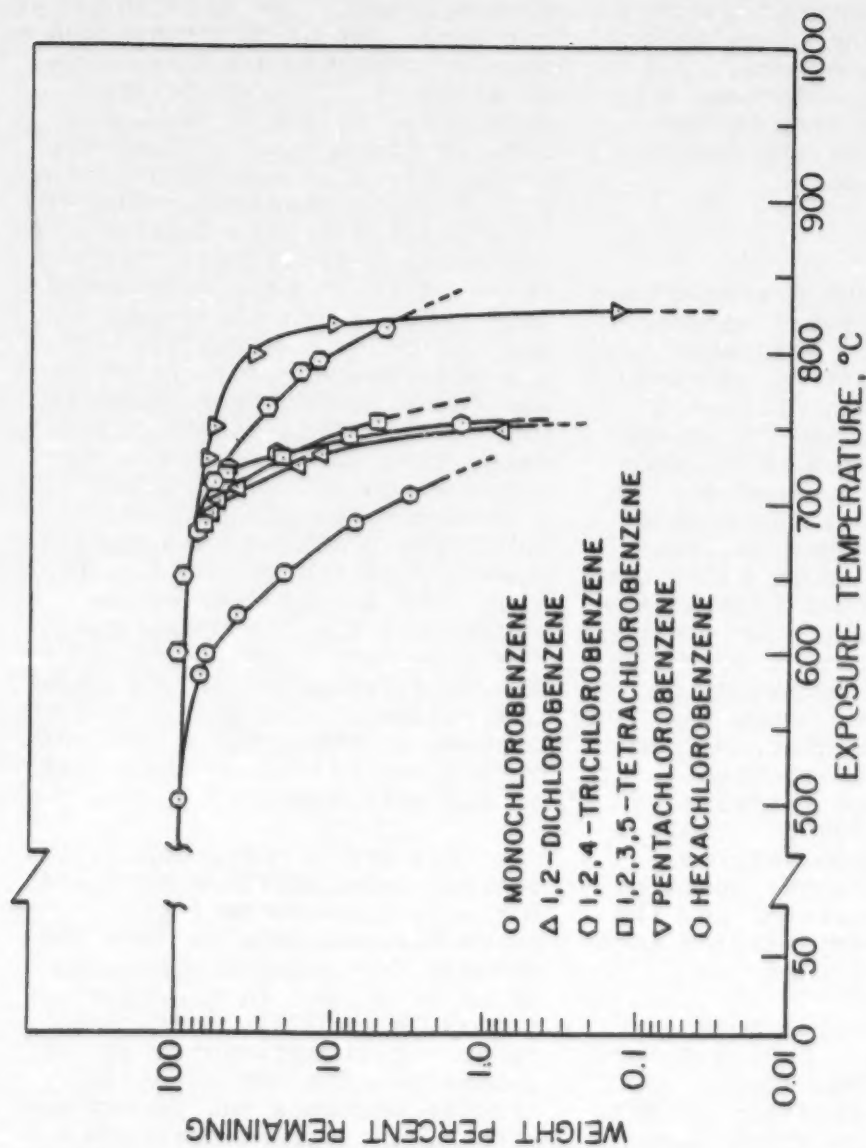


Figure 2. Thermal Decomposition Profiles for Selected Chlorobenzenes in Air at 2.0 Seconds Mean Residence Time.

TABLE 1
THERMAL DECOMPOSITION PARAMETERS
FOR SELECTED CHLORINATED BENZENES IN AIR
AT 2.0 SECONDS RESIDENCE TIME

Compound	Temperature for Onset of Thermal Decomposition °C	Extrapolated Temperature for 99.99% DRE °C
Benzene	610	760
Monochlorobenzene	520	790
1,2-Dichlorobenzene	615	790
1,2,4-Trichlorobenzene	620	795
1,2,3,5-Tetrachlorobenzene	620	800
Pentachlorobenzene	675	840
Hexachlorobenzene	615	880

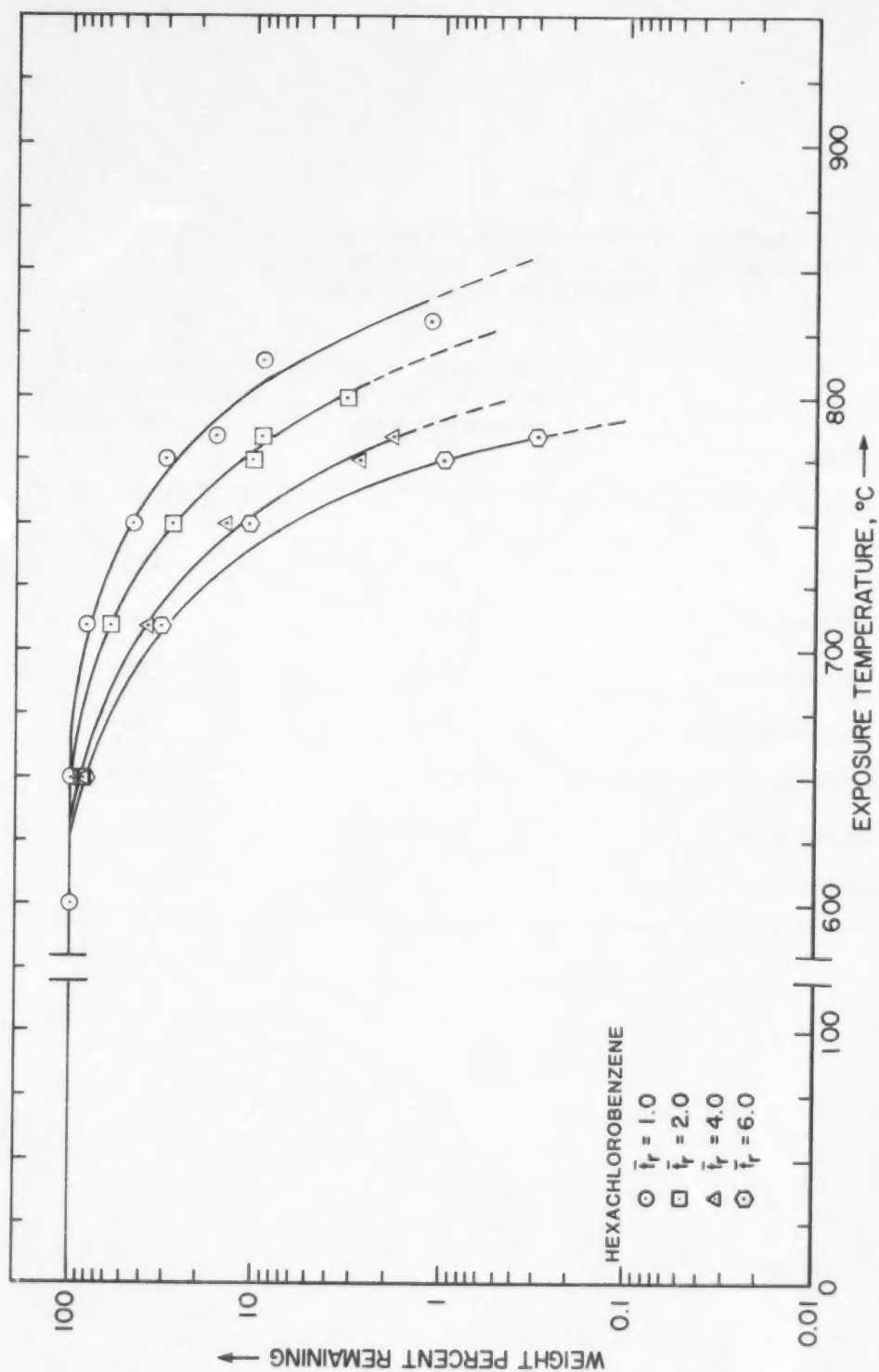


Figure 3. Thermal Decomposition Profiles for Hexachlorobenzene in Air at Mean Residence Times of 1.0, 2.0, 4.0, and 6.0 Seconds.

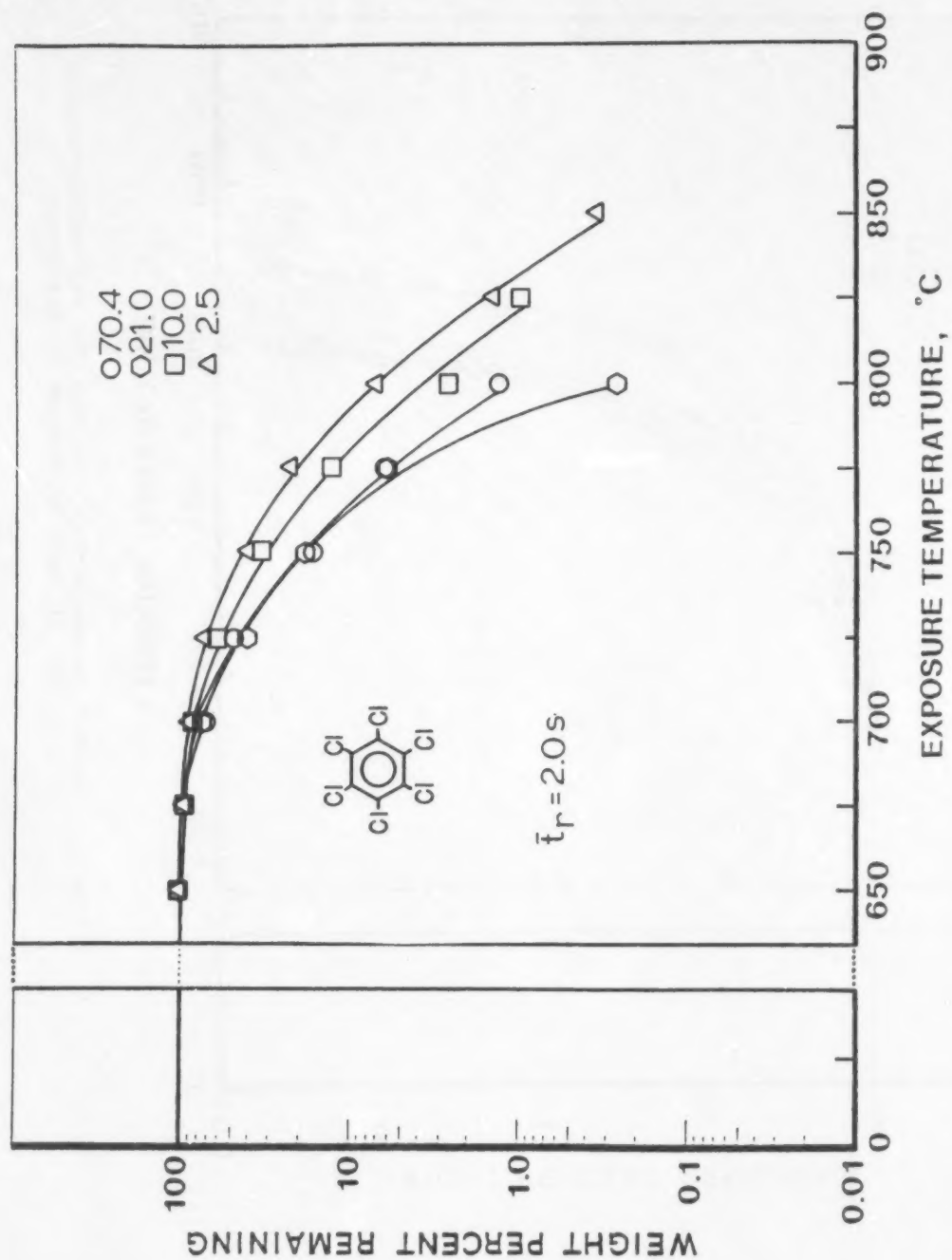


Figure 4. Thermal Decomposition Profiles for Hexachlorobenzene in 2.5, 10, 21, and 70% Oxygen in Nitrogen.

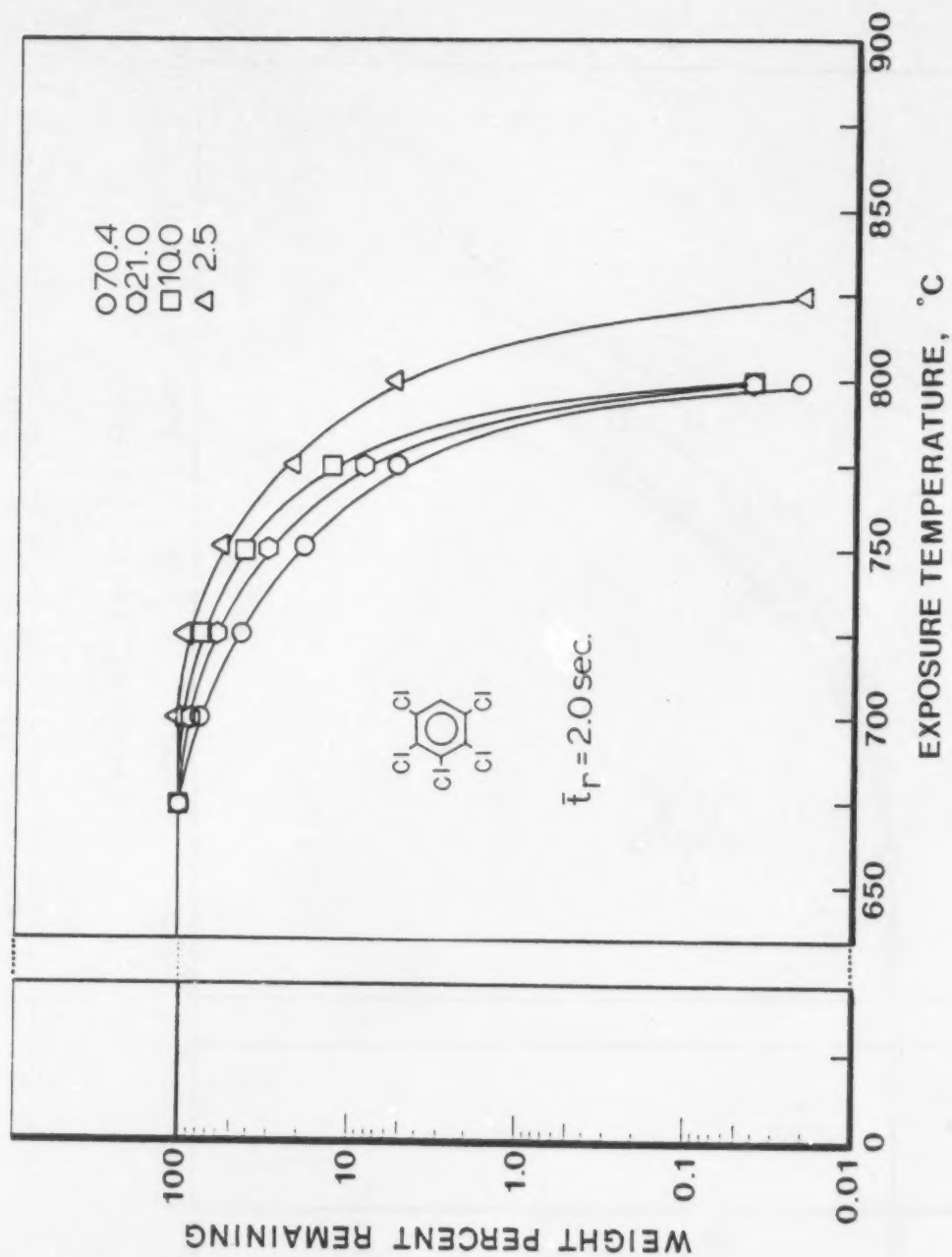


Figure 5. Thermal Decomposition Profiles for Pentachlorobenzene in 2.5, 10, 21, and 70% Oxygen in Nitrogen.

2,2',4',5,5'-PCB, some potentially useful and interesting models can be hypothesized.

$T_{99.99}$ of 880°C ($E_a = 41$ kcal/mole and $A = 2 \times 10^8 \text{ s}^{-1}$).

Discussion

The development of a model for the prediction of thermal destruction efficiencies of hazardous organic compounds is of obvious utility. An equation has been developed to predict the required temperature for 99.99% DE. (6)

$$T_{99.99} = 503 E_a (\ln 0.109 A \bar{t}_r)^{-1} \quad (1)$$

Where: $T_{99.99}$ = the temperature required for 99.99% DE, °K

E_a = the measured activation energy, kcal mole⁻¹

A = the measured Arrhenius coefficient, s⁻¹

$\bar{t}_r$ = the mean residence time, s⁻¹

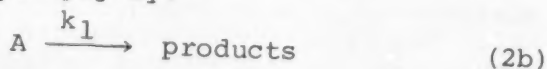
This expression can be used to accurately determine the temperature required for 99.99% DE, at various high temperature zone residence times, for compounds for which the kinetic parameters E_a and A are known. The model explicitly assumes that the disappearance of the parent compound is first order with respect to the parent compound and zeroth order for all other species. For each compound tested thus far, thermal decomposition data taken between $\bar{t}_r = 1.0$ and 6.0 seconds (with more than one percent of the original sample destroyed) has fit first order kinetics with correlation coefficients (r^2) greater than 0.95. The calculated $T_{99.99}$ at $\bar{t}_r = 2.0$ s for hexachlorobenzene is 888°C, compared to the extrapolated

The decomposition of the parent at the temperatures studied can in principle be due to four general mechanisms: unimolecular decomposition, attack by molecular oxygen, chain reactions involving molecular decomposition products, and chain reactions also involving oxygen. The four possible decomposition pathways may be treated with two global mechanisms, one dependent upon the oxygen concentration (oxidation) and a second, dependent on the bond strengths of the parent compound (pyrolysis).

The oxygen dependence of the decomposition of the parent A , may be expressed in terms of the global reaction with oxygen:



while the pyrolysis is given simply by:



This results in the overall kinetic expression for the disappearance of the parent:

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A][O_2]^n \quad (3)$$

where: $[A]$ is the concentration of the parent,

$[O_2]$ is the oxygen concentration, and

k_1 and k_2 are the global rate constants for pyrolysis and oxidation respectively.

Figure 6 presents the experimentally determined reaction order with respect to oxygen as a function of temperature for pentachlorobenzene and hexachlorobenzene. The dependence upon the oxygen concentration for pentachlorobenzene is much more pronounced than for hexachlorobenzene, the latter being almost constant. In the case of pentachlorobenzene, the decomposition would appear to be dominated by oxygen attack at low temperatures while it is much less oxygen dependent at higher temperatures.

The implication of the data thus far obtained on 2,2',4',5,5'-PCB (which was first order in oxygen at 704°C), pentachlorobenzene, and hexachlorobenzene is that the susceptibility to oxygen attack is a function of both the number of hydrogens present in the parent compound and the reactor temperature. This is consistent with a mechanism of oxygen attack through abstraction of a hydrogen radical. The rate of the pyrolysis pathway may be controlled by the strength of the weakest bond.(8) This suggests that the initial decomposition of HCBz (which contains no hydrogens) is dependent on the carbon chlorine bond strength while in pentachlorobenzene and 2,2',4',5,5'-PCB the initial decomposition results from hydrogen abstraction by molecular oxygen.

Summary

The study of the phenomena occurring in the non-flame afterburner region of an incineration system is only one part of the very complex process we know as incineration. However,

one must recognize that the afterburner is the component of the system which allows it to achieve the desired destruction efficiencies. If all gas phase matter were exposed to the nominal conditions of a high-temperature kiln, multiple hearth fluidized bed, or liquid injection incinerator, they would be destroyed with greater efficiency than 99.99%. Unfortunately due to the heterogeneous nature of industrial organic wastes and various nonuniform transport properties through certain portions of incineration systems, there is breakthrough of 'exceptional' molecules which experience less destructive conditions. Thus it is up to the non-flame high-temperature region of the system to destroy these residuals and in fact, control the ultimate DE of the incinerator.

Our data indicate a complex relationship between destruction efficiency, time, temperature, and reaction atmosphere in this region. The time/temperature relationship can be adequately modeled with first order kinetics. However, this relationship of time and temperature to the reaction atmosphere is not so simple.

Our observations suggest that excess oxygen concentrations does not appear to be as important for the thermal degradation of highly chlorinated species as for hydrocarbons. This effect is most pronounced at high temperatures. Based on these thermal decomposition studies, the optimum combination may be very compound specific for chlorinated waste materials.

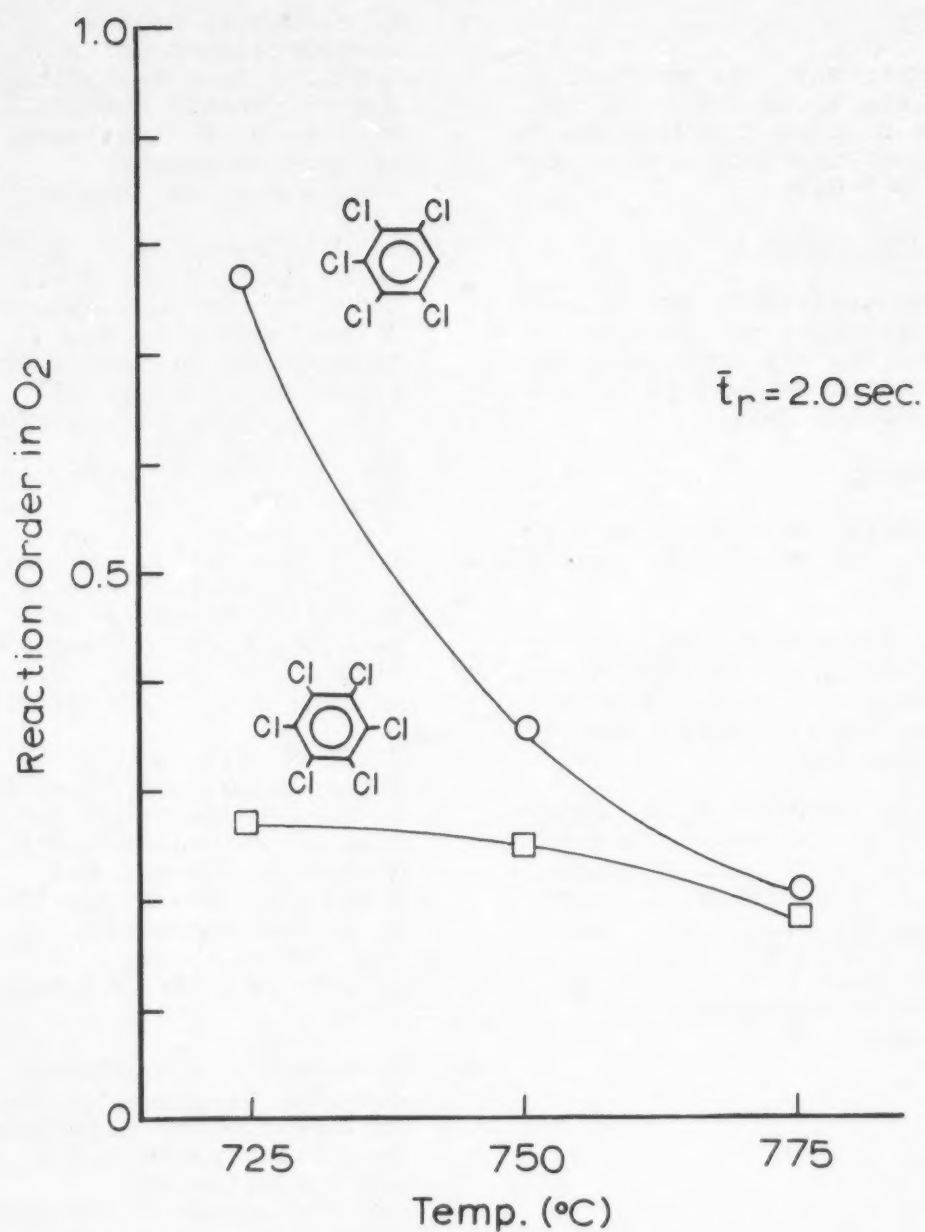


Figure 6. Reaction Order in Oxygen for Hexachlorobenzene and Pentachlorobenzene as a Function of Reactor Temperature.

Credits

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LABORATORY-SCALE FLAME MODE STUDY OF HAZARDOUS WASTE INCINERATION

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ABSTRACT

A research program to study the flame-mode incineration of hazardous waste liquids in laboratory scale reactors is presented. The objective of this study was to supply the flame-mode data that will assist in the evaluation of the applicability of various approaches to ranking ease of incinerability. Two reactors, each emphasizing different aspects of liquid injection incinerator performance, were utilized. Five common liquid waste compounds were selected for testing: benzene, chlorobenzene, chloroform, 1,2-dichloroethane, and acrylonitrile. In the Microspray Reactor, monodisperse waste droplets were injected into laminar postflame gases to study the combined effects of droplet evaporation, droplet-flame stabilization, and flame-zone chemistry on the compound destruction efficiency. A turbulent flow reactor used a commercial spray nozzle to inject an auxiliary fuel, containing dilute test compound, into a commercial spray nozzle to inject an auxiliary fuel, containing dilute test compound, into a swirl-stabilized turbulent-spray flame. In addition to the droplet and chemical effects considered in the microspray reactor, the turbulent flow reactor includes the effect of turbulent mixing on destruction efficiency. This paper outlines the program goals in relation to the incinerability ranking procedure, presents the experimental design, and discusses data.

INTRODUCTION

Permitting procedures for hazardous waste incinerators are defined by the Resource Conservation and Recovery Act (RCRA). A permit to operate is issued after a trial burn has been executed or other appropriate test data obtained which demonstrated that the incinerator satisfactorily eliminated the hazardous compounds when operated under specified conditions. Satisfactory elimination is defined in terms of destruction and removal efficiency (DRE). However, since most hazardous waste streams contain many compounds, a trial burn which involves the measurement of all of them would be prohibitively expensive. Consequently, the trial burn involves the measurement of a

subset of compounds (the principal organic hazardous constituents--POHCs) which are present in the input stream. If the DRE of these POHCs is 99.99 percent or greater, then a permit to operate is granted. Thus, the burden of responsibility rests with the permit writer who must select the subset of compounds (POHCs) based upon concentration and incinerability. This paper summarizes a project which was carried out to examine methods of ranking incinerability.

Several procedures have been proposed to rank incinerability (2), namely:

- The heat of combustion.
- The auto-ignition temperature (AIT).

- A computational approach based upon AIT, compound structure, and other compound-dependent parameters (10,11).
- The temperature necessary for a given destruction level within a given time under dilute premixed conditions ($T_{99.99}$) (4,6,7,10,11).
- Susceptibility of the compound bond structure to attack by flame radicals (16).

These procedures have their merits but fail to take into account all the conditions which may exist in actual incinerators. The heat of combustion, for example, of a particular compound may be insignificant if it is present in small quantities and is mixed with an auxiliary fuel. Some of these procedures do not consider reactions that occur in flames. The times and temperatures which exist under nonflame experimental conditions may be inappropriate for large-scale diffusion flames.

Incinerability defines the relative difficulty with which a compound can be destroyed by incineration. If during the trial burn it is demonstrated that those compounds which are most difficult to destroy have a DRE greater than 99.99 percent, then it is assumed that all the more easily incinerated compounds will have been satisfactorily eliminated. Thus, there is a need for a system which will rank hazardous compounds according to their incinerability and be applicable to all incinerator types and operating conditions. If the ranking system is not generally applicable, then a condition could exist wherein a POHC was eliminated satisfactorily but other hazardous compounds in the waste stream were not destroyed sufficiently. Under these circumstances, a trial burn designed to measure only the POHC would have incorrectly demonstrated the satisfactory operation of the incinerator.

Because of the nature of flames, waste compounds which experience a flame environment are rapidly and effectively destroyed. In a liquid injection incinerator, the waste is destroyed by heat and radical attack produced by the combustion of the waste and an auxiliary fuel (oil or natural gas) in a turbulent diffusion spray flame. Under ideal flame conditions (uniform mixing and high temperatures) the concept of incinerability has little

significance since all hazardous compounds will be completely destroyed. Nonflame thermal decomposition data obtained under dilute premixed conditions (4,6,7,10,11) indicate that temperatures much lower than those encountered in typical incinerator flames will destroy all the organic hazardous waste compounds which have been tested to date. For example, nonflame data indicates that chlorobenzene would decompose to 99.99 percent of its original concentration in 1 sec at 1038°K (11). At temperatures more representative of flames (approximately 2000°K), the time required to obtain the same destruction level is much smaller ($<10^{-13}$ sec) than typical flame residence times (on the order of 10^{-2} sec). Also, because of high reactant concentrations in flames, free radicals which must be present to propagate the flame, will contribute to destruction of the compounds in the flame (15). These free radicals will increase the rate of decomposition above those predicted from dilute decomposition kinetics.

Incomplete destruction of a hazardous waste compound in an actual incinerator must be caused by conditions which allow some of the material to escape or bypass the flame since organic compounds are destroyed rapidly in a flame environment. Most incinerators include long residence time hold-up zones or afterburners to destroy material which is not completely processed by the flame zone. Thus, incinerability must be based not only upon the chemical properties of the compound but also upon its physical properties and their interaction with the incinerator operating conditions because these may influence the failure mode. The term failure mode is used to describe those conditions which might occur in a practical incinerator which preclude complete processing of the waste material by a high-temperature turbulent diffusion flame. Failure may be due to a variety of conditions such as poor atomization, flame quenching by impingement with walls, or poor mixing; thus, it is important to evaluate incinerability under conditions which simulate those failure modes which could occur in practice.

Various phenomena account for the failure of turbulent diffusion flames, typical of those used in liquid injection incinerators, to completely destroy a liquid waste. The destruction efficiency in the flame may be less than quantitative (100 percent) because of any of the

following reasons:

1. Atomization Parameters. When the waste material is injected as a liquid which must be atomized, poor destruction efficiency can result from inappropriate atomization. Droplets which are too large may be produced or their trajectory may be such that they penetrate the flame zone and ignition does not occur.
2. Mixing Parameters. In a turbulent diffusion flame the reactants are supplied separately and reactant contacting takes place via turbulent mixing. Poor mixing can result in low destruction efficiencies because the waste material may not be mixed with oxygen before it escapes from the flame region.
3. Thermal Parameters. The destruction efficiency may be low because flame temperatures are low. This can occur if the calorific value of the waste/auxiliary-fuel mixture is low, heat removal rates are high, or quench rates are high due to mixing with excessive excess air levels.
4. Quenching Parameters. The reactants can be quenched before destruction is complete by heterogeneous or homogeneous phenomena. Mixing can cause quenching as explained above, or the flame may contact a relatively cool surface.

Consequently, it is essential to investigate the concept of incinerability in flames under conditions which could account for a failure to completely destroy the waste compound and are typical of real systems.

The primary goal of the study described in this paper was to compare the incinerability ranking procedures which have been proposed with those measured under flame conditions typical of liquid injection incinerators. The approach utilized was to measure the exhaust compound concentration under different simulated failure modes and to compare the ordering of the compounds to those given by several incinerability ranking procedures. Failure conditions were simulated for all the parameters expected to influence incinerator performance; i.e., atomization, mixing, thermal, and quenching.

To simulate all of them required two reactors. A microspray reactor consisting of a laminar premixed flat flame into which test compounds were injected was used to investigate thermal parameters. A subscale turbulent diffusion spray flame was used to investigate atomization, mixing and quenching parameters. Secondary goals included the generation of fundamental flame mode destruction data necessary to compare flame and nonflame decomposition and to act as a guide for the types of experimentation which are needed to establish an incinerability ranking which could account for different modes of failure.

EXPERIMENTAL APPROACH

Extensive investigations are being carried out at the University of Dayton Research Institute under EPA sponsorship to define the kinetics of waste decomposition in postflame regions (4,6,7). The emphasis of the present study was on the flame zone itself and the impact of failure conditions associated with mixing, thermal, quenching, and atomization parameters on the relative destruction of five compounds. These compounds were selected because they represented a broad range of incinerability as defined by existing ranking procedures. The study was restricted to conditions typical of liquid injection incinerators--no attempt was made to include phenomena associated with waste destruction in beds. Two flame reactors were used to study destruction efficiency under different limiting conditions:

1. A microspray reactor allowed destruction efficiency to be investigated under controlled conditions, using well dispersed droplets in a high-temperature laminar flow background gas.
2. A turbulent flame reactor allowed destruction efficiency to be investigated under more realistic conditions and the conditions could be exaggerated to simulate different failure modes.

This section briefly describes these reactors, the analytical procedures, and the test compound selection. A complete description is available elsewhere (8).

Microspray Reactor

The microspray reactor was employed in this program in order to investigate single-droplet reactions without limitations associated with turbulent mixing. Data from this reactor could be easily interpreted in terms of how thermal parameters influenced compound incinerability in the absence of atomization, mixing, or quenching parameters.

In the microspray reactor, droplets are injected through a laminar premixed hydrocarbon flat flame and react in the postflame gases whose temperature and composition can be controlled. If the reactor is to simulate the conditions which prevail in a liquid spray diffusion flame, it must satisfy the following criteria (1):

- The gas-phase temperature must be in the range of typical flame temperatures (up to 2000°K) and be well-defined and controllable.
- The fuel must be in the form of droplets in the size range (20-200 μm) of typical commercial atomizer performance.
- The droplets should be well-dispersed in a gas-phase environment which is similar to the recirculated products in the near field of a turbulent diffusion flame in order to simulate the contacting between liquid and gas.

The microspray reactor used in this study is similar to the flame reactors used previously in studies of the thermal decomposition of pulverized coal particles and heavy fuel oil droplets (9,14,15) and the characterization carried out in the previous studies confirmed that it satisfied the criteria listed above.

The microspray reactor used in this study is shown schematically in Figure 1. Droplets were injected through the center of a square flame holder constructed of ceramic honeycomb with dimensions 8.9 x 8.9 cm. The flame reactant mixture, either $\text{H}_2/\text{air}/\text{N}_2$ or $\text{CH}_4/\text{air}/\text{N}_2$ was distributed to the honeycomb through a sintered metal plate and burned as a thin flat flame which was supported on the flame holder. The test compound droplet stream was injected through a 1.3 cm diameter opening in the burner center. Almost monosized 38 μm droplets were generated with a Berglund and Liu vibrating orifice technique and the droplet

stream was dispersed by passing the stream through a second orifice and coflowing dispersion gas (9). The composition of the dispersion gas was adjusted so that the stoichiometry including the droplets, was by 100 cm long, stainless steel duct. The exhaust gases from the chimney were directed through a mixing baffle tube prior to a gas sampling port in order to mix the products uniformly.

The microspray reactor was used to investigate the impact of three controllable parameters on the destruction efficiency of five hazardous waste compounds: temperature, stoichiometry, and droplet composition (pure compounds versus mixtures). One potential incinerator failure mode is that the droplet environment (e.g., temperature) may not be sufficient to cause ignition or decompose the waste constituents. In the microspray reactor, the reaction temperature was controlled by varying the amount of diluent nitrogen temperature as measured with a type R (Pt/Pt-30% Rh) thermocouple on the center line of the duct are presented in Figure 2a. Radial temperature profiles (Figure 2b) indicated that the gas-phase temperature across the duct was relatively uniform except near the edges. These measurements were made with the droplet dispersion flow present but

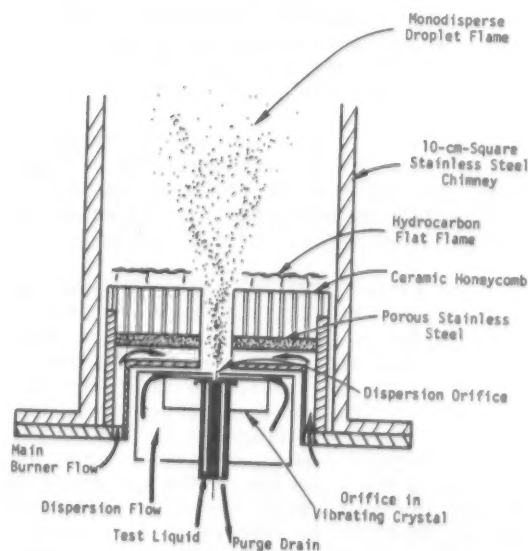


Figure 1. Details of microspray reactor.

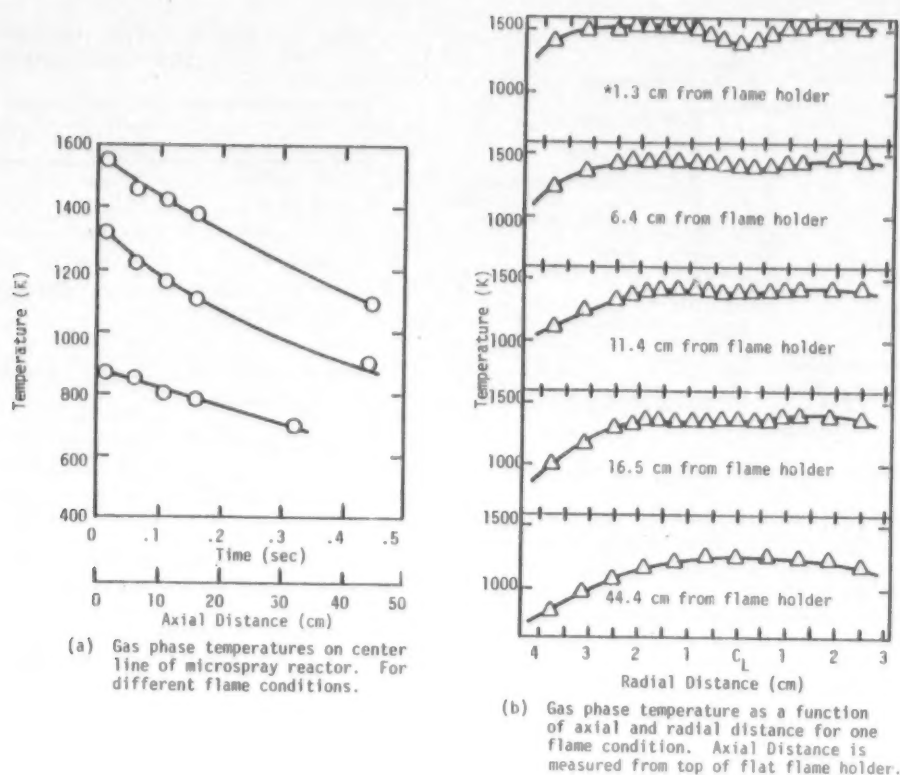


Figure 2. Gas temperature measurements in microspray reactor.

without droplets present. When droplets were injected they were confined to the central zone of the duct (maximum diameter, 3 cm) and were therefore all subject to the same thermal history. The destruction data was determined as a function of the flame temperature which was obtained by extrapolating the axial temperature measurements to the burner face.

Compound effects were also investigated for two extremes in stoichiometry, rich and lean. For rich conditions, the flat flame was operated with deficient oxygen (stoichiometry ratio = 0.83) and the gas used to disperse the test compound droplets was identical to the flat flame feed gas. Under these conditions, the droplets evaporated and thermally decomposed with no oxygen available for oxidation. For lean conditions, the flame stoichiometry was adjusted to provide 10 percent more oxygen than was necessary to burn both the flame gas and the test compounds. In this case, the droplets were dispersed with air.

When droplets were injected into a rich flame, they were virtually invisible to the naked eye. However, when droplets were injected into a sufficiently hot ($>850^{\circ}\text{K}$) lean flame, the individual droplet flames became visible. Droplets ignited due to heat transfer from the flat flame gases and flame radical attack on the vaporized material from the droplet. The ignited droplets appeared as blue streaks due to the chemiluminescence resulting from flame reactions around individual droplets. The visual appearance of droplet flames was utilized as an indication that the flat flame temperature was sufficient to ignite the test compound droplets.

Turbulent Flame Reactor (TFR)

The second reactor consisted of a turbulent diffusion spray flame contained in a cold-wall chamber and is shown schematically in Figure 3. The subscale flame was designed to simulate many aspects of commercial practice relevant to liquid injection

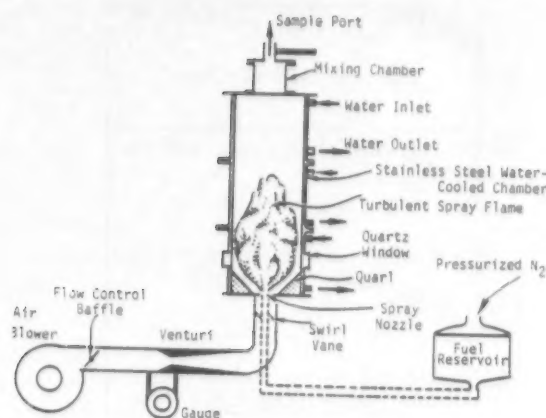


Figure 3. Turbulent flow reactor.

incinerators including swirl, recirculation, a broad droplet size distribution and a high variation in droplet number density. Since the flame was contained in a cold-wall chamber, the flame gases were rapidly cooled. Consequently, there was little opportunity for postflame destruction of the waste compounds and the destruction efficiencies were only dependent upon flame conditions.

The waste compounds were mixed with auxiliary fuel (either heptane or diesel oil) and atomized using a commercial pressure jet spray nozzle (Delavan WDA-600). Air entered through interchangeable swirl vanes placed in the annular space around the nozzle and the burner throat. The resulting swirl-stabilized flame was contained in a water-cooled stainless steel cylindrical chamber 30 cm in diameter and 90 cm long. The lower section of the chamber was equipped with an ignition port, observation ports, and a castable refractory quartz to prevent corner recirculation. Combustion products from the chamber were homogenized in a mixing chamber prior to sampling.

The normal operating condition (see Table 1) for the TFR was selected based upon commercial practice, visual flame stability, low exhaust CO (<75 ppm) and total hydrocarbon (<20 ppm) and high destruction efficiency of hazardous waste compounds. Under these conditions, extremely high destruction efficiencies (>99.995 percent) for all of the test compounds were measured. Several variations from the normal operating conditions were investigated, which had little influence on the high flame destruction efficiency of the hazardous waste constituents. These included auxiliary fuel type (No. 2 fuel oil), burner throat velocity and test compound concentration (up to

TABLE 1. NORMAL OPERATING CONDITIONS FOR TURBULENT-FLAME REACTOR

NOZZLE	Delavan Pressure Jet, Hollow Cone, 60° Spray Angle Model WDA-600-1.5
NOZZLE PRESSURE	103 psig
AUXILIARY FUEL	Heptane
FUEL FLOW RATE	1.4 gm/sec (11 lb/hr)
AIR FLOW RATE	14.3 l/sec (1830 ft ³ /hr)
BURNER THROAT VELOCITY	7.1 m/sec (23.3 ft/sec)
BURNER SWIRL NUMBER	1.0
EXCESS AIR	30%
BURNER HEAT RELEASE RATE	38 kW (131,000 Btu/hr)
TEST COMPOUND CONCENTRATION	3% by Mass
EXHAUST CONCENTRATIONS	CO: 75 ppm Total Hydrocarbons: 20 ppm
DESTRUCTION EFFICIENCY OF TEST COMPOUNDS	>99.995%

25 percent). Variations which did result in significant deterioration in both flame performance and destruction efficiency and were used to investigate compound effects under failure conditions included:

- Low excess air
- High excess air
- High excess air and low load
- Poor atomization quality
- Quench coils within flame

Test Compounds

Five compounds, listed in Table 2, together with some of their properties were selected as representative of liquid organic hazardous wastes. All the compounds are listed in the 1980 RCRA regulations, Part 261, Appendix VIII (16). The compounds were chosen to represent a broad range of incinerability based on the most commonly proposed ranking procedures. They cover greater than 90 percent of the range in heats of combustion for the listed compounds (.13 to 10.14 kcal/gm). Since a direct comparison between nonflame thermal decomposition rankings and the flame mode destruction was an objective of this study, compounds were selected for testing for which nonflame data was available. In addition, the selection also took into account the National Bureau of Standards ranking system, a range of auto-ignition temperatures and a variety of molecular structures. Two of the compounds are aromatic, one is a highly chlorinated methane, another is a chlorinated ethane and one contains nitrogen.

TABLE 2. TEST COMPOUNDS AND COMPOUND PROPERTIES

COMPOUND	Boiling Point (K)	T99.99 (K) ①	Autoignition Temperature (K) ②	Heat of Combustion (kcal/gm) ③	Heat Rank ④	Evaporation Time (msec) ⑤
Chloroform	355	290 ⑥	-	0.75	18	9.0
1,2-Dichloroethane	356	931	686	3.0	28	11.9
Benzene	352	1006	836	10.03	4	14.4
Acrylonitrile	351	1002	754	7.93	-	20.9
Chlorobenzene	405	1037	911	6.6	3	10.8

① Temperature required for 99.99% DE at $t = 1$ sec ⁽¹¹⁾② Data as reported by Lee ⁽¹¹⁾

③ Data from Guidance Manual, Mitre Corp.

④ Incinerability Ranking Based on Bond Strength and Susceptibility to Radical Attack from Tsang, ⁽¹⁵⁾. Rank 1 is most difficult to incinerate.⑤ Calculated time for 100 μ m droplet to evaporate at 1000°K ⁽⁸⁾⑥ Data after Duvall ⁽³⁾

Measurement Techniques

The measurement of waste concentration in the sample stream for both reactors involved the adsorption from a known amount of exhaust gas onto Tenax organic sorbent (8,13). The exhaust gas sample was first passed through a heated (200°C) particulate filter, and then through a water-cooled Tenax cartridge held at 20°C (see Figure 4a). The cartridge was on 8 cm long by 1.3 cm diameter Pyrex tube packed with 1 gm of Tenax. After adsorption, the cartridge was placed in a specially designed aluminum block heater immediately upstream of the GC column (Figure 4b). The column employed was a 1-meter-long 0.3 cm OD Teflon tube packed with acetone-washed Porapak-Q. A temperature of 150°C was found to be sufficient to desorb the test compounds into the packed column. The GC oven temperature was subsequently temperature-programmed to 120°C to separate the compounds.

The use of Tenax for concentrating the sample and then thermally desorbing provided the necessary rapid turnover of samples with sufficient separation and sensitivity. The breakthrough volumes of all the test compounds were directly measured and were found to be greater than the utilized sample volumes (8). Benzene and 1,2-dichloroethane were not separable by the Porapak-Q column and hence mixtures containing both

compounds were avoided. Under the normal operating conditions specified in Table 1, the exhaust concentration of individual compounds was measurable down to 1.5 ppb. This corresponds to a destruction efficiency in the TFR of greater than 99.995 percent.

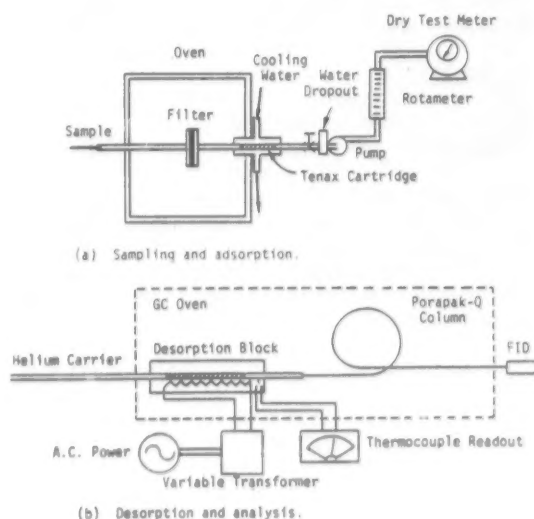


Figure 4. Tenax-GC sampling and analysis technique for measuring exhaust concentrations of compounds selected for testing.

MICROSPRAY RESULTS

The microspray was used to investigate the impact of thermal parameters for three conditions:

- Fuel-lean--oxygen available to oxidize test compounds.
- Fuel-rich--no oxygen available to oxidize test compounds.
- Mixtures of compounds and pure compounds.

The other failure mode parameters (atomization, quenching, and mixing) cannot be effectively investigated in the microspray reactor and were investigated in the turbulent flame reactor.

Figure 5 presents data for two mixtures of four compounds shown separately in Figure 5a and 5b. In these tests, 38 μm droplets of the two mixtures were injected separately into a lean (10 percent excess oxygen) $\text{H}_2/\text{Air}/\text{N}_2$ flame with different flat-flame temperatures. Exhaust concentrations of the individual test compounds were measured and the data are shown in Figure 5 in terms of the fraction of each compound remaining versus the measured flat-flame temperature. This temperature is determined by extrapolating the axial temperature measurements to the burner face and is the highest temperature of the flat-flame gas. Under these excess oxygen conditions, droplet flames were observed for both mixtures for flat-flame temperatures in excess of 850°K. However, droplet ignition was observed at slightly lower temperatures for one mixture probably due to the substitution of compounds. When the flat-flame temperature is greater than the ignition temperature of the specific compound mixture, the exhaust concentration of the test compounds were below the detection limit of the analytical technique which indicated a destruction level in excess of 99.995 percent.

Calculations using nonflame kinetics (8) indicate that almost no decomposition should occur below 800°K for the residence times (~ 1 sec) available in the microspray reactor. However, as shown in Figure 5, significant destruction was measured at flat-flame temperatures below 800°K. This destruction at low flat-flame temperatures is probably due to a local increase in temperature around droplets and flame radical attack. Above the visual droplet ignition point, all the compounds were destroyed,

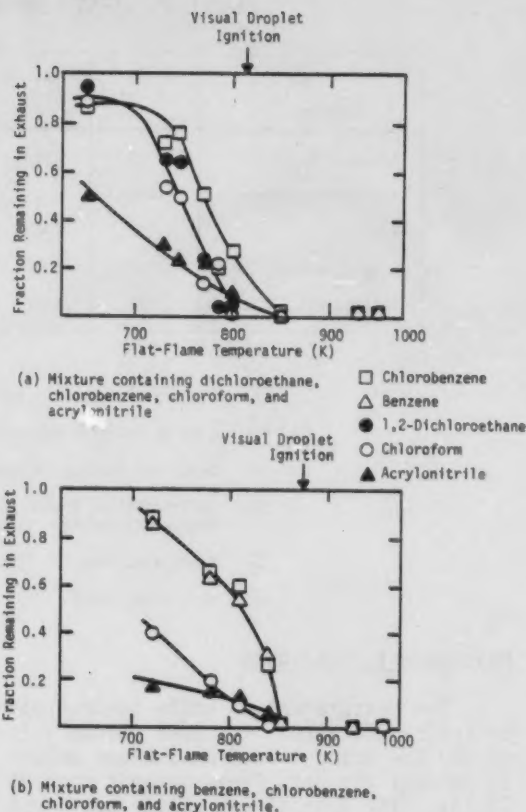


Figure 5. Fraction of test compound remaining in exhaust when 38 μm droplets of mixtures of compounds were injected into lean (10% excess oxygen) H_2/air flames as function of flame temperature.

but below the ignition temperature the fraction destroyed depended upon the compound. At low flat-flame temperatures for the mixture containing dichloroethane, chlorobenzene had the highest concentration in the exhaust followed by dichloroethane, chloroform, and acrylonitrile. At flat-flame temperatures just below the droplet ignition point, again chlorobenzene was found to be the most difficult compound to be eliminated but the other compounds showed some rearrangement in ranking; but the effect of compound type is small. When benzene was substituted for dichloroethane (Figure 5b), chlorobenzene remained the most prominent compound in the exhaust followed by benzene, chloroform, and acrylonitrile. Again, just below ignition there was some reordering of compounds with chloroform becoming the

easiest to eliminate. These data indicate that for single droplet oxidative conditions where the temperature is too low for droplet ignition, a particular order of compounds does exist in terms of the fraction remaining in the exhaust. This order is chlorobenzene, benzene, 1,2-dichloroethane, chloroform, and acrylonitrile. However, this order changes as the temperatures reach the ignition point. The ordering just below ignition is identical to the ordering suggested by T_{99.99} and auto-ignition temperature (see Table 2).

When 38 μ m droplets of pure compounds were injected into oxygen-rich lean flame products, the droplets were observed to ignite at different temperatures. For example, visual ignition for chloroform droplets was observed at 860°K, while dichloroethane ignited at 850°K, acrylonitrile at 800°K, and chlorobenzene at 740°K. Benzene had the lowest ignition temperature and was observed to ignite at temperatures below 600°K. For pure compounds, the destruction is controlled by droplet ignition. The observed ignition temperature does not agree with any proposed incinerability ranking procedures, although the heat of combustion criteria is almost the same with the exception that acrylonitrile and chlorobenzene are reversed.

The absence of oxygen was the third failure mode investigated with the micro-spray reactor. Droplets of equal molar mixtures of compounds were injected into fuel-rich (stoichiometric ratio = 0.83) H₂/air/N₂ flames of different temperatures. In these tests, the oxygen was rapidly and completely consumed by the hydrogen in the flat flame so that no oxygen was available to oxidize the test compounds. The fraction of each compound remaining in the exhaust as a function of the flat-flame temperature is shown in Figure 6. Even with mixtures, the temperature required to destroy the compounds, 1050°K, was found to be very similar to the T_{99.99} temperatures of the individual compounds (920 to 1037°K; see Table 2) and were much higher than those required if droplet ignition occurred (Figure 5). The fractional destruction was strongly dependent upon flame temperature. A difference between the compounds was observed only at a temperature just below the flat-flame temperature required for complete destruction. At that temperature, the compound that was most predominant was chlorobenzene, followed by benzene, chloroform, and acrylonitrile.

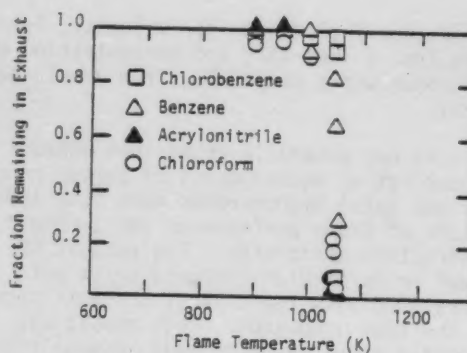


Figure 6. Fraction of test compound remaining in exhaust when 38 μ m droplets of mixtures of compounds were injected into rich (stoichiometric ratio = 0.83) H₂/air flame as a function of flame temperature. Incinerability order at 1050°K is chlorobenzene, benzene, acrylonitrile, and chloroform.

This ranking was identical to that measured for the low-temperature oxidation data (Figure 5). The nonflame T_{99.99} did identify the temperature range required for complete destruction and the most predominant compounds (chlorobenzene and benzene); however, acrylonitrile and chloroform are reversed from the T_{99.99} ranking. Pure compounds were not tested under fuel-rich conditions although similar results to the mixture data is expected.

TURBULENT FLAME REACTOR RESULTS

The turbulent flame reactor was operated and tested under a number of conditions. However, many of these conditions resulted in high destruction efficiency of all the test compounds. Only those parameters resulting in significant deterioration of destruction efficiency are presented here. Data on high destruction levels are presented elsewhere (8). The conditions investigated in the turbulent flame reactor which had a strong influence on destruction efficiency were primarily associated with three failure parameters:

- Atomization parameters--poor atomization quality.
- Quenching parameters--quenching on cold surface.
- Mixing parameters--low excess air
--high excess air
--low heat-release rate

Those parameters found to be of less

importance included burner velocity, fuel type (No. 2 fuel oil) and concentration of hazardous waste compounds (from 3 to 25 percent).

It was generally found that exhaust concentration measurements of carbon monoxide and total hydrocarbons were good indicators of flame performance and compound destruction efficiency. The exhaust CO level in particular appeared to be well correlated with the exhaust concentration of the test compounds. This result was expected since the high heat removal rates in the TFR emphasized flame performance over postflame reaction. Since CO is an intermediate in the oxidation of hydrocarbons to CO_2 (13), it is directly linked with combustion efficiency. Therefore, an examination of the relative CO levels for each failure condition indicates the overall combustion efficiency which can be compared to the destruction efficiency of the hazardous waste compounds. The relationship between exhaust CO, total hydrocarbons measured by the flame ionization detector, and destruction efficiency measured for a mixture of compounds is shown in Figure 7. The maximum DRE (>99.995 percent) was measured at 30-40 percent excess air, which corresponded to the minimum in both exhaust CO and hydrocarbon.

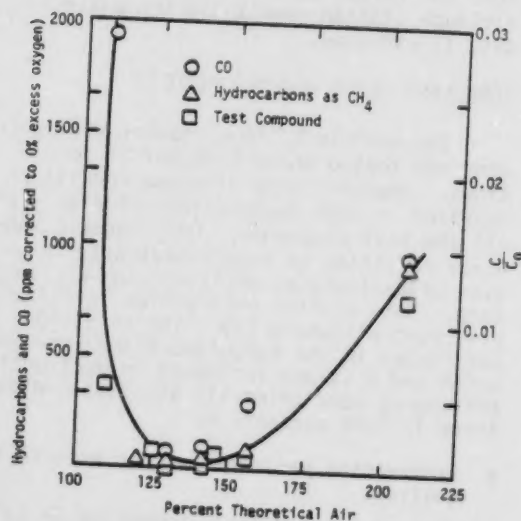


Figure 7. Exhaust CO and total hydrocarbons and fraction of test compound remaining in exhaust as a function of theoretical air (constant air velocity, variable load, equal molar mixture of chloroform, benzene, chlorobenzene, and acrylonitrile added 3 percent by weight to heptane).

Figure 8 presents data obtained with the TFR at high heat-release rates (164,000 Btu/hr). Very high destruction levels (>99.995 percent) were measured for all compounds at 20 percent excess air at this heat-release rate with the exception of benzene. It is possible that benzene was a product of incomplete combustion of either the auxiliary fuel or one of the test compounds (e.g., chlorobenzene). The actual source of the benzene whether it is a product of incomplete combustion or an indication of incomplete benzene destruction, has not been determined. Benzene is a possible intermediate in the formation of soot which was observed in the flame in the form of luminosity, especially at low excess air levels. Because of the relatively large amounts of heptane present (97 percent) only a small conversion of heptane to benzene is required to account for the exhaust levels of benzene measured at this low excess air condition. However, the benzene could also be the result of a simple transformation of chlorobenzene.

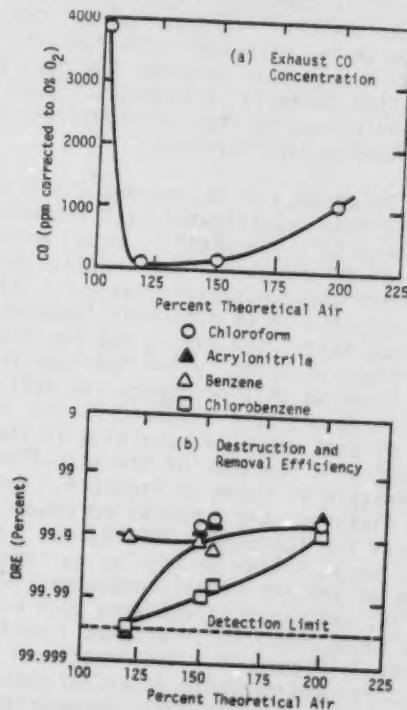


Figure 8. Impact of theoretical air on CO and DRE from turbulent flame reactor. Incinerability order at 150 percent T.A. is chloroform, acrylonitrile, benzene, and chlorobenzene (constant load = 164,000 Btu/hr; variable air flow rate and burner velocity; equal molar mixture of compounds added 3 percent by weight to heptane).

At higher excess air levels (>150 percent theoretical air) the exhaust concentrations of CO and the test compounds increased. This is probably due to lower flame temperatures and increased quenching which can occur when large amounts of unheated air are present. The lowest DRE level obtained for these high heat-release rates (164,000 Btu/hr) was 99.9 percent. The compound differences were small but measurable at 150 percent theoretical air. Chloroform was the most predominant test compound in the exhaust followed closely by acrylonitrile and benzene with chlorobenzene having the highest destruction efficiency. This particular order, which was found to exist for a number of failure conditions tested with the turbulent flame reactor does not agree with any of the proposed rankings in Table 2, although the heat of combustion did identify the most predominant compound (chloroform).

The data obtained at low heat-release rates (90,000-155,000 Btu/hr) are shown in Figure 9. This data set was achieved by lowering the fuel flow rate from the nominal operating conditions (Table 1) while maintaining the air flow constant. This drop in load and increase in theoretical air resulted in significant increase in the fraction of the waste compounds in the exhaust. Under this failure condition, chloroform and benzene had similar high exhaust concentrations followed by 1,2-dichloroethane and similar low-exhaust concentrations for acrylonitrile and chlorobenzene.

The data presented in Figure 10 indicate that atomization parameters had a significant impact upon compound destruction. In these tests, a nozzle designed for 1.5 gal/min was operated at .75 gal/min dropping the pressure from 161 psig to 40 psig. This increases the mean droplet size (5) and affects fuel air mixing causing some of the large droplets to escape the flame. The highest compound exhaust concentrations were measured under these poor atomization conditions. However, the order of compounds was found to be identical to other failure conditions for the TFR such as high excess air at high loads, low excess air at low loads, and quench coils. The chloroform was found to be the most predominant compound followed by benzene, acrylonitrile, and chlorobenzene.

A water-cooled copper coil was placed directly within the flame in the TFR to provide an extreme case of flame quenching in order to investigate destruction efficiencies

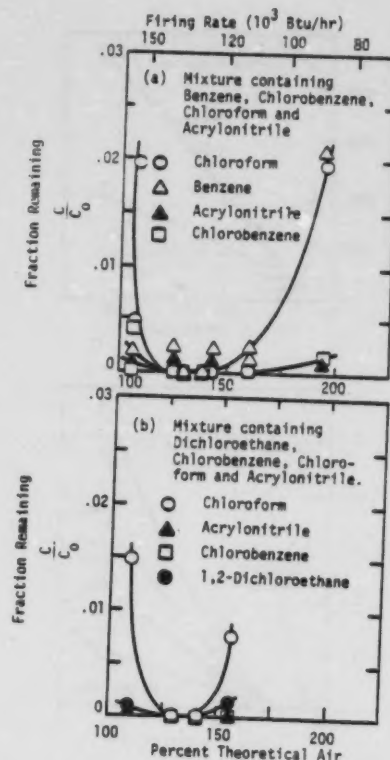


Figure 9. Impact of theoretical air and load on fraction of test compounds remaining in exhaust of turbulent flame reactor (constant air velocity, variable load 155,000-90,000 Btu/hr; equal molar mixture of compounds added 3 percent by weight to heptane).

under this mode of failure. In this failure condition test, the coil acted to cool the flame and supplied a surface area for reactants to quench. The presence of the quench surface increased both CO and the test compound concentration (see Figure 11). The order of the compounds was similar to other failure conditions with chloroform being the most predominant and chlorobenzene the least predominant compound in the exhaust. However, the positions of acrylonitrile and benzene were reversed from the order found in other failure modes.

DISCUSSION

The combustion of hydrocarbon fuels in turbulent diffusion flames results in relatively high flame zone temperatures (between 1600 and 2000°K) and residence times are on the order of 0.1 seconds. If the waste compounds investigated in this study experience

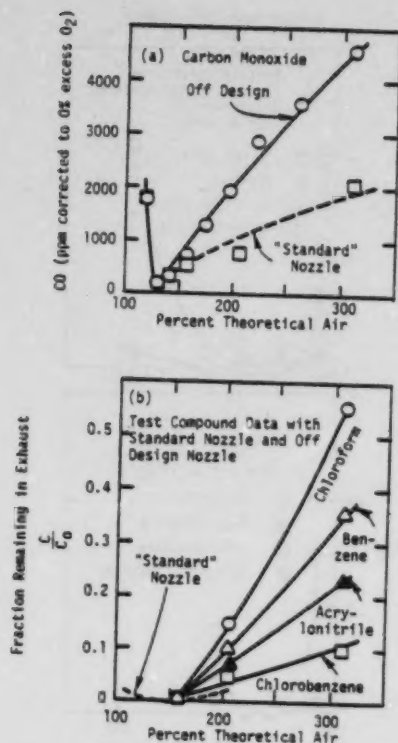


Figure 10. Impact of atomization quality on CO and fraction of test compounds remaining in exhaust of turbulent flame reactor. Incinerability order is chloroform, benzene, acrylonitrile, and chlorobenzene (constant air velocity, variable load 155,000, 55,000 Btu/hr; equal molar mixture of compounds added 3 percent by weight to heptane).

these conditions, then they would be quantitatively destroyed. The results of this study agree with this hypothesis. Turbulent diffusion spray flame and a laminar reactor burning single droplets were capable of destruction efficiencies greater than 99.995 percent. In the case of the turbulent flame reactor under optimized conditions (stable flame, low CO and total hydrocarbon), the compounds were destroyed mainly in the flame because postflame decomposition was minimized due to the fact that the flame was contained by cold walls. Consequently, it can be concluded that a flame is an extremely efficient mode of destroying waste compounds and the concept of incinerability under these conditions has little value. If everything is destroyed, it is not possible to rank compounds in terms of difficulty or ease of destruction. Consequently, a series of experiments were designed to assess incinerability

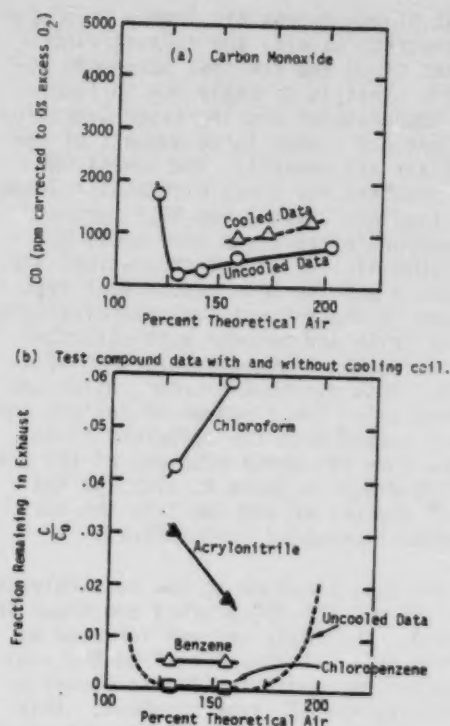


Figure 11. Impact of cooling coil placed in flame on CO and fraction of test compound remaining in exhaust of turbulent flame reactor. Incinerability order is chloroform, acrylonitrile, benzene, and chlorobenzene (constant air velocity; load = 114,000 Btu/hr; equal molar mixture of compounds added 3 percent by weight to heptane).

under several limiting conditions which might typify the failure mode of practical liquid injection incinerators.

The microspray reactor investigated those conditions associated with single droplet combustion in the absence of complications due to turbulent mixing. It was selected in order to study thermal effects separated from turbulent mixing and atomization. The temperature required to ignite droplets of hazardous waste under oxygen-rich conditions in the laminar premixed flat flame reactor was found to be low (850°K) in comparison to typical flame temperatures (1500-2000°K). Above the ignition temperature, the droplets were visually observed to ignite and the compounds tested were quantitatively (>99.995 percent) destroyed. Even in the absence of oxygen, the microspray data indicated that low temperatures

(~1000°K) were required for complete destruction even without droplet ignition. These data were consistent with the high destruction efficiencies achievable in a turbulent diffusion spray flame environment of the TFR. The TFR was operated at high heat removal rates by operating with water-cooled walls in order to minimize postflame reactions and mixtures up to 25 percent by weight of the test compounds were investigated. Even in the absence of significant postflame decomposition, destruction efficiencies which corresponded to the detection limits of the analytical systems (99.995 percent) were achieved for all the compounds tested. In the turbulent flame reactor, a direct relationship was observed between overall combustion efficiency as indicated by exhaust CO and hydrocarbon emissions and the destruction of the test compounds. Conditions which minimized the CO concentration in the exhaust gases also maximized destruction efficiency. Under all failure conditions investigated, exhaust CO concentration increased when the test compound concentration increased. These results suggest the feasibility of using exhaust CO and potentially total hydrocarbons to monitor the performance of liquid injection incinerators once the conditions giving the maximum destruction efficiency have been defined.

The incinerability or ordering of the compounds was found to depend on the actual failure condition which caused the inefficiency. When both the microspray and the turbulent flame reactor were operated under conditions which simulated failure modes of practical incinerators, measurable differences in the destruction efficiency of the five test compounds were obtained. For example, chlorobenzene was the most difficult to eliminate in the microspray when the temperature was too low to ignite the droplets, but was the least difficult to eliminate for a variety of failure conditions in the TFR such as poor atomization quality.

Figure 12 presents a series of bar graphs which allow a comparison between incinerability as defined by the various failure modes and the rankings indicated by procedures based upon T_{99.99}, heat of combustion, the NBS method, and AIT. The bar graph shows the concentrations measured in the experiment normalized so that the most predominant compound shows full-scale and the lesser concentrations are expressed as a percentage of that maximum concentration.

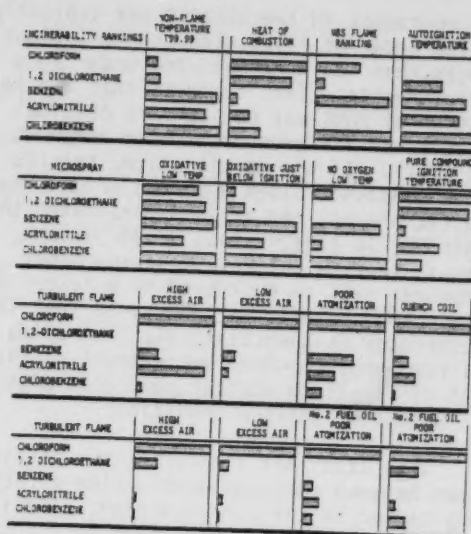


Figure 12. Comparison of proposed ranking techniques and concentration measured in the experiments under flame failure conditions normalized so most predominant compound shows full scale.

This approach gives an indication of the measured magnitude of the difference in destruction efficiency between compounds. A comparison of these relative concentration measurements with proposed incinerability ranking techniques demonstrates that none of the proposed techniques agree with the data for all failure conditions. However, some of the ranking procedures were found to be appropriate for specific failure conditions. For example, the nonflame thermal destruction (T_{99.99}) and AIT procedures both agreed with the compound concentration measurements when the temperature was below droplet ignition temperature and under oxygen-deficient conditions. Heat of combustion was found to correlate the pure compound data when the microspray was operated below droplet ignition temperature. In most instances, chloroform was the most difficult compound to incinerate for the failure conditions investigated with the TFR, and this was anticipated by only one of the four ranking techniques--heat of combustion.

Although measurable differences in the destruction efficiency of the five test compounds were obtained, the differences were not large under any of the conditions tested. For the most part, the variation in the concentration (between highest and lowest) of

the compounds in the exhaust was typically of the order of five, although variations larger than ten were measured under some circumstances. This suggests that the selection of POHC may not be very critical because the differences between compounds are small. If the permit writer selects three compounds based upon two or more ranking techniques, and it is demonstrated that their DRE is greater than 99.99 percent, then it is very unlikely that any other compounds will be destroyed to a lesser degree. Nonetheless, to be assured that the incinerator is quantitatively destroying all compounds requires measurement of the most difficult to destroy compounds under all potential failure conditions.

This study has identified the differences between compound destruction efficiency caused by failure conditions associated with the flame zone. High destruction efficiencies have been demonstrated in the flame alone. However, many incinerators are equipped with postflame hold-up zones and after-burners in order to achieve additional thermal decomposition of compounds which escape the flame zone. In order for an incinerator to fail to destroy a compound, the material must both escape the flame and the temperature be too low in the postflame hold-up zone to destroy the compound (less than $T_{99.99}$). The differences in the concentration of compounds in the exhaust of the incinerators is associated with both the flame and nonflame zones. The thermal decomposition which occurs in the postflame zone can alter the ranking in the exhaust. However, this occurs only if the temperature in the postflame zone is between the $T_{99.99}$ of the two compounds. For example, the IFR data indicated that chloroform with a $T_{99.99}$ of 930°K is the most likely compound to escape the flame and chlorobenzene is the least likely with a $T_{99.99}$ of 1038°K. If the postflame zone temperature is less than 930°K, then the flame zone ordering will prevail in the exhaust. If the temperature is greater than 1038°K, then both compounds are quantitatively destroyed. However, if the temperature is between 930 and 1038°K, then chloroform is destroyed leaving chlorobenzene intact. Hence the postflame rank will prevail if, and only if, the temperature in the postflame is between the two compounds; in this case, a 100 C temperature range. The temperature in the postflame zone is not uniform and the temperatures referred to above are minimum temperatures for a residence time of one second.

It was not the purpose of this study to ascertain why destruction efficiency under flame conditions can be compound and failure mode specific. More detailed measurements are needed to provide further information. It could be associated with flame inhibition due to the presence of halogens which are known to reduce burning rates. Under quenching conditions, these effects could be enhanced. The formation of products of incomplete combustion (PICs) as a consequence of the partial destruction of the waste compound, was not investigated. An alternate method of assessing incinerability could be based upon the potential to form PICs which are themselves hazardous.

CONCLUSIONS

1. Under optimum conditions, flames are capable of destroying hazardous waste compounds with very high efficiencies (greater than 99.995 percent) without the need for long residence time high-temperature postflame zones or after-burners.
2. Reduced flame destruction efficiencies are the result of operation under some failure mode such as poor atomization, poor mixing, or flame quenching.
3. Incinerability, or ordering of compounds in terms of their relative destruction efficiency, is dependent on the actual failure condition which caused the inefficiency.
4. Optimum conditions for destruction of hazardous waste compounds in turbulent diffusion spray flames correspond to minimal exhaust CO and total hydrocarbons.
5. No one incinerability ranking system appears to predict correctly the relative destruction efficiency of the five compounds tested for all failure conditions investigated. However, several rankings did correctly predict relative DE for specific failure conditions.
6. More data is required on other compounds and other failure conditions more appropriate to different types of hazardous waste incinerators to fully determine the limitations of incinerability ranking systems and develop an appropriate incinerability ranking methodology.

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THE PACKAGED THERMAL REACTOR SYSTEM:
DEVELOPMENT AND APPLICATION

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ABSTRACT

In view of the urgent need for thermal decomposition data to guide the safe incineration of hazardous organic materials and industrial wastes, the University of Dayton's Environmental Sciences Group has developed a simple Packaged Thermal Reactor System (PTRS). The PTRS can rapidly, easily, and safely determine the relative thermal stability for organic substances under a wide variety of temperatures, residence times, and gaseous atmospheres. In addition, the PTRS is quite sensitive, as the level of 99.99% destruction can often be measured directly. Also the PTRS is small and quite compact, making it easy to use in almost any installation.

In this paper the design, development, and application aspects of the prototype PTRS are discussed.

INTRODUCTION

As controlled high-temperature incineration plays an increasing role in the permanent disposal of hazardous organic wastes there is a growing need for basic thermal decomposition data concerning these materials. Closely

related to this is the availability of suitable analytical instrumentation which can provide these data.

Since 1969, the Environmental Sciences Group of the University of Dayton Research Institute has been actively involved in the design

and development of thermal instrumentation systems. This paper will discuss the various aspects of the latest in a series of thermal instrumentation systems designed and developed at the University. This new system is referred to as the Packaged Thermal Reactor System (PTRS).

BACKGROUND

The early thermal decomposition research activities at the University of Dayton were aimed at developing special instrumentation to study the thermal decomposition properties of organic polymeric materials. In 1974, the emphasis shifted to developing special thermal systems which could address the thermal decomposition behavior of industrial organic wastes, toxic organic materials, and other environmentally sensitive substances. The first such system was the Discontinuous Thermal System (DTS). This was a relatively simple instrumentation assembly consisting of a heatable sample inlet region, a high-temperature quartz tubular reactor, an effluent trap for collection of unreacted parent compounds along with various reaction products, and a detached programmed-temperature gas chromatograph. The DTS provided valuable information with respect to the thermal decomposition of various pesticides, e.g., Kepone, Mirex, and DDT. [1]

From an instrumentation standpoint, this particular system was important for another reason. Specifically, it laid the groundwork for more sophisticated studies by identifying

those variables which are of concern to laboratory-scale thermal decomposition studies. These variables are listed in Table 1. Also, while conducting experiments using the DTS the importance of the formation of products of incomplete combustion (PICs) was clearly revealed.[1] This important finding led to the development of the Thermal Decomposition Analytical System (TDAS).

In principle, the TDAS is similar to the DTS in that it consists of a thermally programmable inlet region that is connected to a quartz tubular reactor with a cryogenic in-line trap for capture of the effluent products from the reactor. In reality, however, the TDAS is a far more sophisticated system and has evolved to the point that it bears little resemblance to its predecessor. The TDAS, unlike the DTS, is a truly continuous system. Connected downstream of the cryogenic trap is an LKB 2091 GC-MS which is used for analyzing the effluent products. This unit also has a dedicated minicomputer which processes the data and aids in the interpretation of the mass spectra.

With its GC-MS and dedicated minicomputer, the TDAS proved to be a powerful tool for the investigation of gas phase thermal decomposition behavior. Over the past four years, this unit has been used to study the thermal decomposition of numerous pesticides, industrial organic wastes, and pure compounds. The TDAS is a very sophisticated system and by its nature it is also a relatively expensive system to assemble and maintain. With that in mind, we set out to design an instrument with

TABLE 1

GAS PHASE
THERMAL DECOMPOSITION VARIABLES

EXPOSURE TEMPERATURE

RESIDENCE TIME

COMPOSITION OF ATMOSPHERE

TEMPERATURE VARIATIONS

CHAMBER PRESSURE

RESIDENCE TIME DISTRIBUTION

capabilities similar to the TDAS but which incorporated recent technological advances at a much reduced cost. This led to the development of the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system[3].

As with the TDAS, the TDU-GC incorporated several improvements over its predecessor. In particular, the TDU-GC's sample inlet region was designed to be more versatile with respect to the different types of samples which can be analyzed. The most significant change was replacing the LBK 2091 with a Varian Vista series programmed temperature high-resolution gas chromatograph. The versatility and operating characteristics of this particular GC, particularly its ability to operate at cryogenic temperatures, expanded the analytical capabilities of the system significantly.

Since it became operational in late 1981, the TDU-GC has shown that it can perform many of the same tasks as the TDAS. The major difference between the two instrumentation assemblies is that while the TDU-GC can detect the presence of PICs, to actually identify them would require further analysis. However, a TDU-GC system may be assembled for about one-third the cost of a TDAS.

As work with the TDAS and the TDU-GC systems progressed, researchers became aware of the enormous demand for data concerning the thermal stability of both pure compounds and complex industrial organic wastes mixtures. Events and discussions at a recent hazardous waste

incineration conference [4] clearly pointed out the urgent need to determine thermal decomposition behavior for a very large number of toxic organic compounds. Eventually, hundreds of different organic compounds may need to be tested. Accordingly, analytical instrumentation is needed which can rapidly screen the thermal decomposition properties of various principal organic hazardous constituents (POHCs) prior to subjecting them to controlled high-temperature incineration. In view of the urgency of this situation, a design was conceptualized for a relatively simple instrument called the Packaged Thermal Reactor System.

Concept for the Packaged Thermal Reactor System

The goals for the PTRS were to design a system which could rapidly and safely determine the destruction efficiency (DE) for an organic material at a given residence time, exposure temperature, and flowing gaseous atmosphere. This instrument should also be small, compact, and relatively portable so that it can be used as part of a mobile field unit or as part of a permanent installation. Finally, it should be an inexpensive unit to assemble and maintain. The concept of such an instrument is presented in block diagram form in Figure 1 and is shown schematically in Figure 2.

The schematic shown in Figure 2, describes one version of the originally proposed PTRS.[5] The various components within the dashed-line boundary represent the packaged

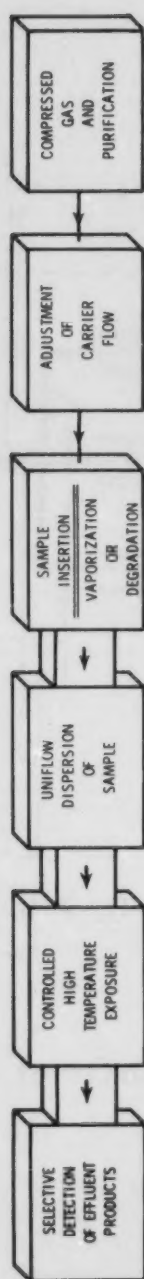


Figure 1. Block Diagram of the Packaged Thermal Reactor System.

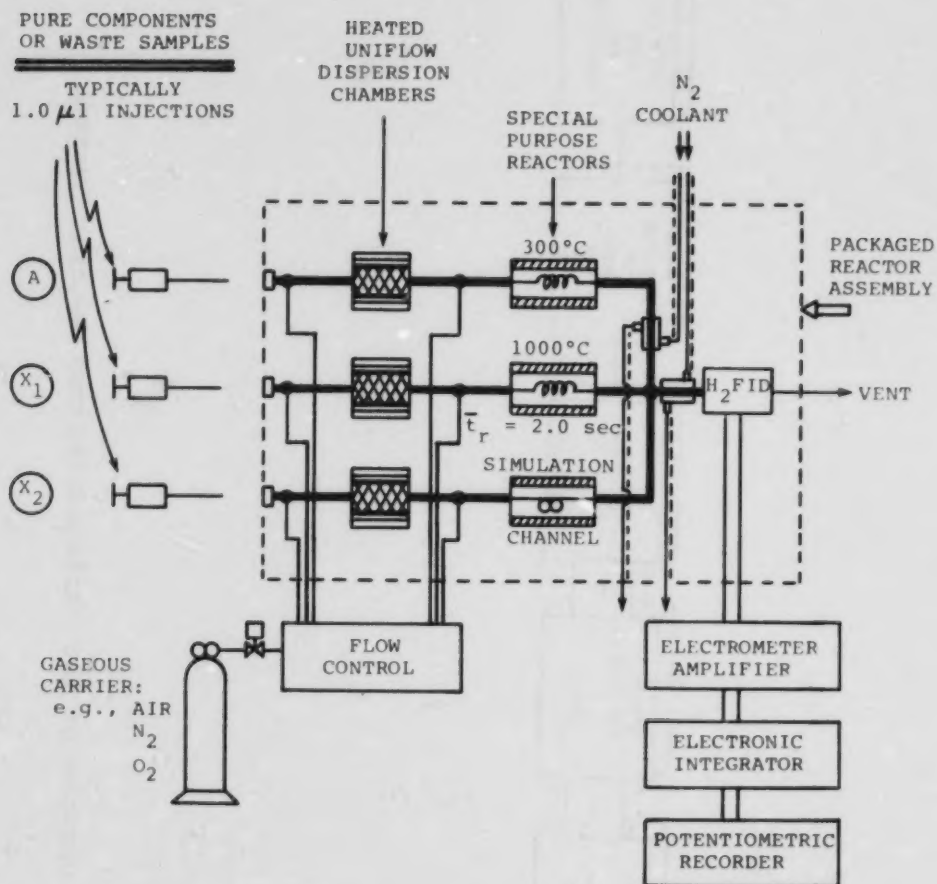


Figure 2. Conceptual Schematic of the Packaged Thermal Reactor System.

reactor assembly. The components outside the boundary are typically found in almost every chemical instrumentation laboratory. An analyst who has been conducting gas chromatographic analyses could readily operate this unit. In addition, once this unit has been installed in a laboratory, the thermal decomposition data can be obtained very quickly. A single determination should take less than ten minutes; and an extremely small sample can be used to minimize safety problems.

In Figure 2, it is seen that localized cooling is an option that can be used for condensing and concentrating organic substances that have passed through the high-temperature reactors. The same localized cold regions of the transport path can also be heated rapidly to release the trapped organic substances and thereby pass them on downstream to the exit location as narrow concentrated zones.

The design of the packaged reactor will also permit the use of interrupted flow techniques. Such an arrangement permits the use of atmospheres with differing oxygen concentrations. Also, with this reactor assembly, tests can be made with almost any type of flowing gas, e.g., air, oxygen, humid atmospheres, hydrogen, or even low levels of chlorine.

Before going further into the details of the uses for the PTRS, it would be desirable to discuss the characteristics of one of the major components of this system which is often overlooked, namely the hydrogen flame ionization detector (HFID).

The Hydrogen Flame Ionization Detector

One of the most useful detectors that can be used with a packaged thermal reactor system is the HFID. This particular device came into existence in 1958 as a sensitive detector for sensing extremely low levels of hydrocarbon. It was apparently conceived and studied simultaneously by several researchers [6,7]. Essentially, this detector has undergone only minor revision since its introduction, and these refinements have been with respect to enhanced electronics with accompanying signal handling techniques.

Today the HFID is probably the most readily available gas chromatographic detector in laboratories throughout the world. It is also the major component in total hydrocarbon analyzers. The HFID has excellent sensitivity in that it can respond to 10⁻¹² grams per second of an organic substance. This detector can be used for sensing a broad range of concentrations as it has a linear dynamic range of between 10⁴ and 10⁷ (depending upon design and associated electronics). For organic compounds, the HFID is a destruction device, as all gas phase species must pass through a flame that operates at approximately 2,200°C. This is a beneficial characteristic with respect to the safety of personnel using this device with hazardous organic materials.

The hydrogen flame ionization detector responds to all compounds containing CH groups, but fails to respond to a number of common inorganic compounds. The chemicals in the

following list exhibit essentially no response to the HFID.

rare gases
hydrogen
oxygen
nitrogen
oxides of carbon
oxides of nitrogen
ammonia
water
silicon tetrachloride
silicon tetrafluoride
trichlorosilane
hydrogen sulfide
hydrogen chloride
sulfur dioxide
carbonyl sulfide
carbon disulfide

A very interesting observation can be made concerning the response to hydrocarbon and halocarbon compounds. However, it will not respond to the final combustion products of hydrocarbons, i.e., H_2O , CO_2 , HCl , etc. This is an important observation with respect to incineration studies and the associated evaluation of the completeness of thermal decomposition or combustion.

If one admits a pure component sample to the transport channel* of the packaged thermal reactor and senses the total effluent with an HFID and its associated electronics, one can obtain total response counts for the unreacted sample. Then, if the same quantity of sample is subjected to another channel set for higher temperature exposure, the response of the surviving

*Channel A of Figure 2 would have adjustable transport temperatures of between $200^{\circ}C$ and $500^{\circ}C$.

organic species can be measured. Thus, the extent of decomposition, combustion, etc., for a given high-temperature exposure can be readily evaluated. In short, by using a packaged thermal reactor system, the calculation for DE (in percent) can be obtained as follows:

$$DE = 100 \left\{ 1 - \left(\frac{R_X}{R_A} \right)^n \right\} \quad (1)$$

Where R represents the integrated response from the respective reactor channel (see Figure 2). This is a very convenient method for determining the relative thermal decomposition behavior of POHCs.

There are several additional features of the HFID which make it especially suited as the primary detection device for a PTRS. The detector is not affected to any great extent by subtle changes in flow rate or other physical parameters which often have profound effects on other types of gas chromatographic detection devices. Also, the response from the detector is practically independent of the simultaneous elution of non-responding species with compounds that do respond to the HFID. For example, the detection of low levels of organic compounds in the presence of massive quantities of CO_2 has little effect upon the resultant output signal from this device. In short, the presence of H_2O , HCl , and large concentrations of other non-responding substances will not adversely affect the detection of low-level concentrations of organic materials.

The HFID is also ideally suited for conducting thermal decomposition tests in pyrolytic atmospheres such as nitrogen, helium, argon, and so forth. This detector can permit studies using low levels of water in the carrier and can also function very nicely with carbon dioxide or hydrogen as the carrier gas [8,9]. Now let us return to the discussion of the PTRS and its application.

Application of the PTRS

Figure 2 shows that the PTRS reactor unit is in fact made up of three sub-units, each of which is a miniature thermal reactor system in its own right. The first channel, referred to as Channel A in Figure 2, is a low to moderate-temperature reactor and this channel is maintained at approximately 300°C to obtain quantitative transport of the sample to the detector. Since no thermal degradation of the sample occurs in this channel, it is used to obtain the total integrated response for an unreacted inserted sample. This, of course, corresponds to a DE of 0%.

The second channel, designated as X₁ in Figure 2, is a conventional narrow-bore high-temperature quartz tubular reactor. Physically this channel is identical to Channel A except in this case the temperature of the reactor may be as high as 1,000°C. By comparing the total integrated response obtained from this channel to that of Channel A, the DE may be easily calculated

The third channel, noted

as X₂ in Figure 2, is a special high-temperature channel that differs greatly from the other channels in that the reactor itself is of a dramatically different geometry. The reactors in Channels A and X₁ are narrow-bore quartz tubes that have been formed into helical coils. These narrow-bore gas flowpaths produce residence time distributions which are narrow and symmetrical. However, Channel X₂ generates a broad and highly skewed residence time distribution.

The configuration of the PTRS as shown in Figure 2 is intended primarily for experimentally determining the DE of organic materials. From the basic drawing of the packaged thermal reactor system (Figure 2), it is evident that the DE can be readily obtained by merely comparing the integrated responses from Channel A and Channel X₁ [See Equation (1), page 10]. This calculation would apply for the thermal testing of pure organic substances as well as complex mixtures of hydrocarbons. However, when a multi-family chemical sample is to be subjected to thermal decomposition studies, e.g., a waste stream sample that contains both hydrocarbons and chlorinated hydrocarbons, a different detection mode could be used, as shown in Figure 3. In this situation, a parallel arrangement using the HFID and the Hall Electrolytic Conductivity Detector (HECD) can provide the same type of information, i.e., the determination of destruction efficiency. The HECD is basically an elemental detection device that responds selectively to the chlorine, nitrogen, and

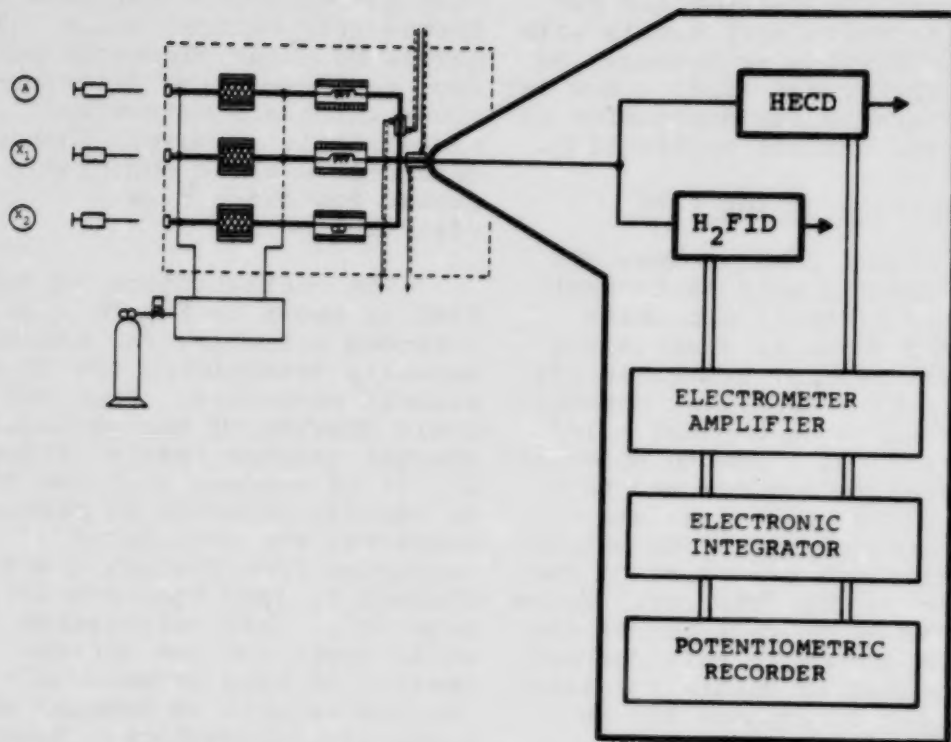


Figure 3. Conceptual Schematic of the Packaged Thermal Reactor System Equipped with Parallel Detectors.

sulfur generated during the course of these thermal exposures. The procedure under which these particular analyses would be conducted is slightly different in that cold trapping is used for these determinations.

Another modification of this PTRS is shown in Figure 4. In this version there is no detector in the system as it is now a preparative unit. Very simply, a collection trap has been placed at the exit of the assembly, and the samples that have passed through the selected reactors can now be trapped for further examination and analysis using other types of analytical techniques, such as liquid chromatography, high-resolution gas chromatography, and gas chromatography-mass spectrometry. Since highly toxic decomposition products can be generated during certain high-temperature exposures a protection trap has been included in this preparative unit.

The availability of a preparative system, such as shown in Figure 4, has considerable value in that sizable quantities of special thermally prepared samples could be readily obtained. This capability would permit sophisticated analyses of important collected products, i.e., products of incomplete combustion. In addition, such a preparative thermal unit could be used to generate samples which could eventually be tested for special toxicological properties, e.g., mutagenic activity, etc.

The Prototype PTRS

The primary objective

associated with designing and fabricating a "prototype" PTRS was to evaluate the validity of the basic concept. More specifically, it was necessary to determine if it was possible (and practical) to construct a reasonably compact multi-channel assembly for measuring the DE of organic materials under a wide range of test conditions.

The PTRS as shown in Figure 5 is a two compartment instrument consisting of a reactor assembly unit and a control unit. The control unit contains all of the gas flow controllers, temperature controllers, and temperature monitoring equipment. The reactor assembly houses all of the reactors, dispersion chambers, the detector, and all of their associated furnaces and heaters. A schematic of the interior of the reactor assembly unit is shown in Figure 6.

The operation of the PTRS may best be explained by following through each step outlined in Figure 1 while referring to Figures 5 and 6. The first step is to select and adjust the appropriate carrier gas. The PTRS was designed to operate with a 50 psig source of any non-corrosive gaseous atmosphere. The carrier enters a distribution manifold within the control unit, which supplies gas to all six of the flow control valves (see Figure 6). The control valves used in the PTRS operate by maintaining a fixed pressure drop across a laminar flow element. By using different restrictor elements, these controllers may be operated over a very large range of

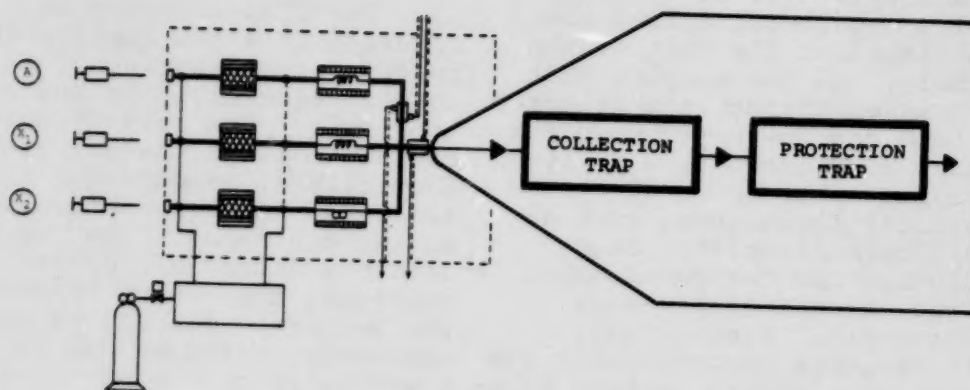


Figure 4. Conceptual Schematic of the Packaged Thermal Reactor System Equipped with a Preparative Unit.

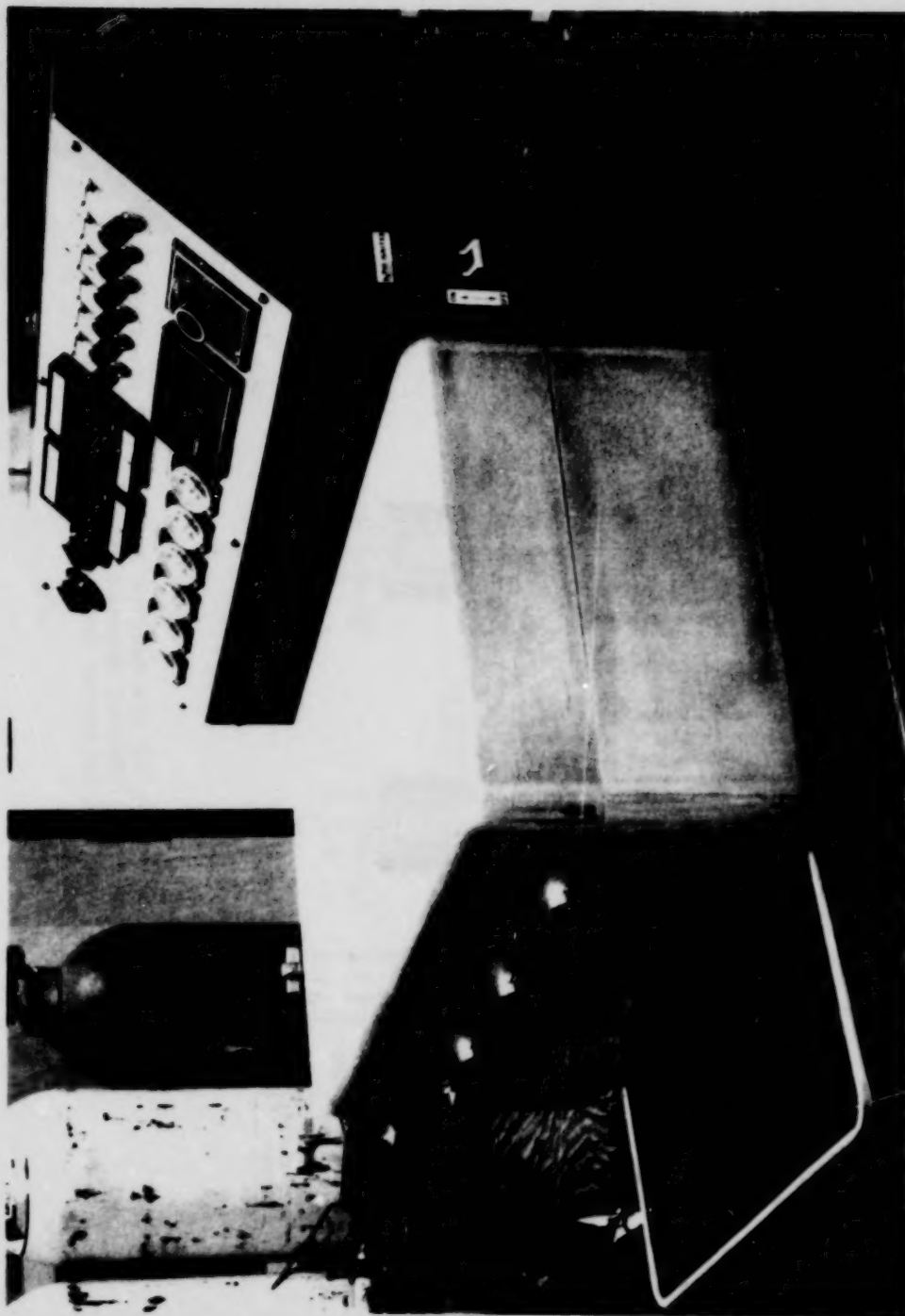


Figure 5. Photograph of the Prototype Packaged Thermal Reactor System. Note: The Reactor Assembly is to the Left (front) and the Controller Assembly is to the Right (rear).

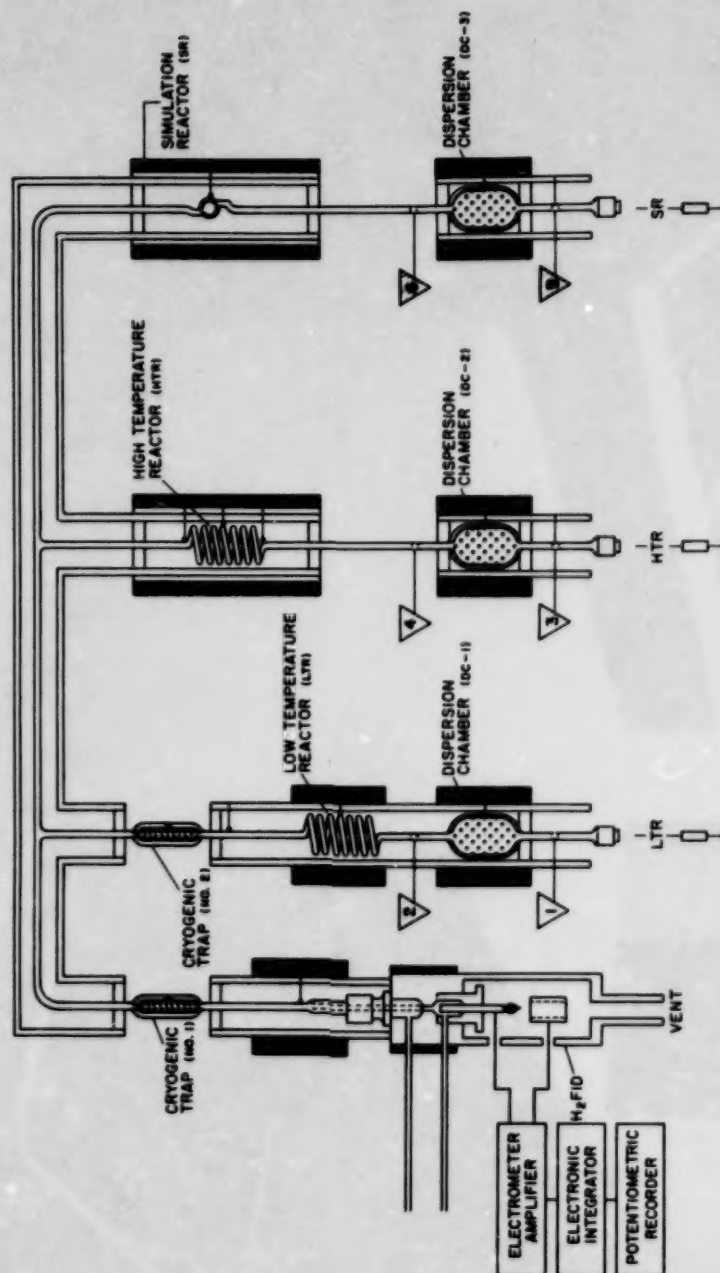


Figure 6. Schematic of the Reactor Assembly of the prototype Packaged Thermal Reactor System. Note: The Inverted Triangles Denote Carrier Gas Inlet Points.

gas flow rates.

Figure 6 shows that there are two carrier gas lines supplying each channel, one purges the dispersion chamber, the other is used to supply auxiliary make-up carrier. By controlling the ratio of the flow rates within these two lines the operator can control the inlet sample concentration profile to the reactor without affecting the total flow of carrier. By using extremely small dispersion chamber purge rates the inlet profile to the reactor will be very dilute and may be hundreds of seconds wide. Since the mean residence time in the reactor is typically 2.0 seconds, this results in a concentration profile within the reactor which is nearly uniform and at all times is highly dilute. This arrangement gives the operator complete control over the conditions under which the experiment is to be performed.

After the carrier gas has been adjusted so the total flow to each reactor will give the desired residence time, the operator must set the various heaters to the desired temperature. In all there are ten heaters to be set and 21 thermocouples are used to monitor the conditions within the reactor assembly. The dispersion chambers, transport lines, Channel A reactor, and HFID heaters may be heated from ambient to 400°C. In normal operation these are set between 200°C and 300°C. The cryogenic traps may be controlled from -130°C (by purging with chilled nitrogen gas) to +300°C. Under normal

conditions these are also set between 200°C and 300°C. The reactors of Channels X₁ and X₂ are normally operated from 300°C to 1,000°C.

Now that the level of dispersion, the residence times, and the various exposure temperatures have been set, the instrument is ready for the ignition of the HFID and the conducting of a thermal decomposition test. Since the PTRS is fitted with standard GC septa, normal syringe injection techniques are used. Sample sizes vary from 0.1 to 5.0 µl for liquid samples, and from 1.0 to 100 µl for gas phase samples. Upon injection the sample is deposited at the entrance to the dispersion chamber. These chambers have been packed with fine mesh Pyrex glass beads. (48% void volume.) This assures complete mixing of the sample with the gaseous carrier.

As the sample is swept from the dispersion chamber, it is augmented by the make-up carrier and transported to the reactor. To reduce the residence time within this transport region the tubing bore is reduced from 1.0 mm I.D. to 0.5 mm I.D. The two narrow-bore tubular reactors are constructed of 2.0 mm I.D. fused quartz tubing. To give a reasonable path length and still have small over-all physical dimensions, these two reactors are configured in the form of helical coils. The actual path length of each is about 40 cm while the coils are only 8 cm in length and 3 cm diameter. The Channel X₂

reactor is in the form of a 1.0 cm I.D. sphere with the entrance and exit tubes located tangential to the sphere and on opposite sides. The exit of each reactor is once again of the small 0.5 mm I.D. quartz tubing. Through the combination of the small bore inlet and outlet tubes the small physical size of the reactors, and the use of small (10 cm) ceramic heaters, the sample is exposed to nearly square-wave thermal pulse, the duration of which may be accurately calculated and easily controlled.

The effluent products from the reactor are carried downstream where they are either cryogenically trapped (this may be necessary to concentrate the effluents when extremely dilute inlet streams are used) or transported directly to the HFID. When the effluent trapping mode is selected, the trap is maintained at cryogenic temperatures until all of the condensable effluent has been captured. The trap may then be heated at 300°C/min. to release the effluent products and they are quickly passed into the detector. After obtaining the total integrated responses from Channel A and the respective high-temperature channel, the DE can then be readily calculated.

Figure 7 shows several examples of thermal decomposition curves generated using the PTRS. All of these data were taken with a mean residence time of 2.0 seconds in air. Note that in all cases the thermal decomposition was followed very near to the 99.99% level of destruction.

Summary and Future Work

The prototype PTRS unit has demonstrated that a small thermal decomposition system can be built. Thus far, research results indicate that the PTRS will meet or surpass all goals with respect to its performance. The specific features of this prototype unit are summarized below.

- The PTRS is small and compact. The entire unit is smaller than some gas chromatographs.
- The PTRS is easy to use. A technician with GC experience can operate the unit.
- The PTRS is fast. Experience has shown that a single determination may be taken in as little as four minutes.
- The PTRS is versatile. The unit can analyze almost any material which responds to the HFID. Also, the PTRS can operate at temperatures up to 1,000°C and with any non-corrosive atmosphere.
- The PTRS is sensitive. In most cases the 99.99% DE may be measured directly.
- The PTRS is safe. Typically .25µl gas samples are used.

Further work on the present PTRS unit will explore its capabilities and limitations. After a complete evaluation of the prototype PTRS (in each of its various modes) it will be used to obtain thermal decomposition profiles for organic substances which are of environmental concern.

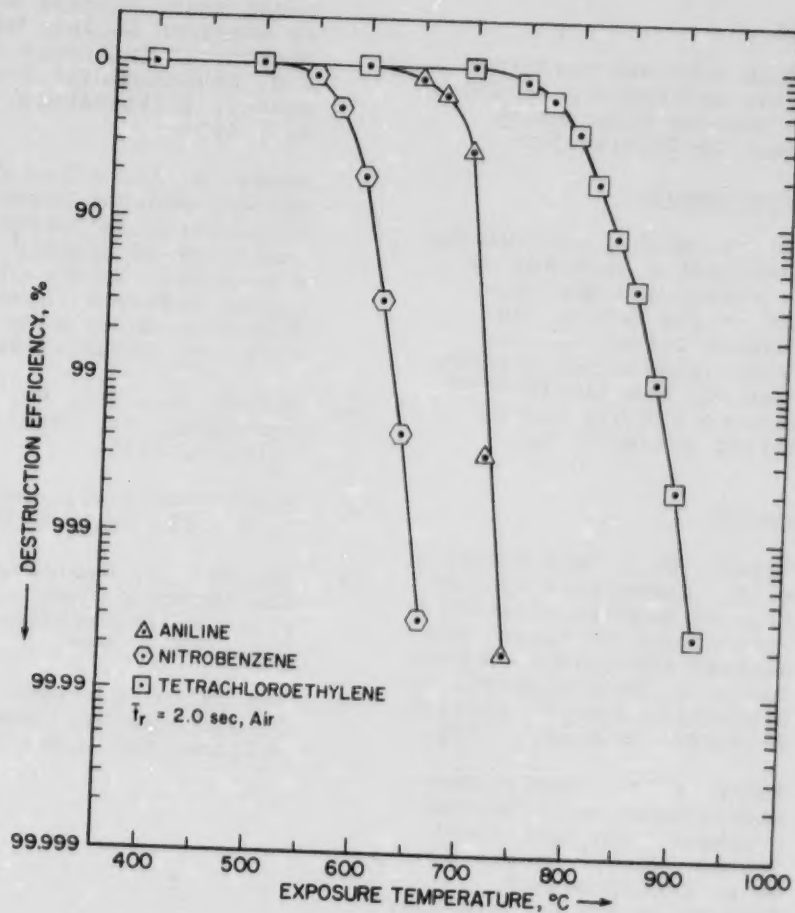


Figure 7. Three Examples of Typical Packaged Thermal Reactor System Data.

Future activities will include the development of a second generation PTRS that will emphasize compactness, portability, and versatility with respect to measuring DES.

Credits

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INCINERABILITY CHARACTERISTICS OF SELECTED CHLORINATED HYDROCARBONS

Ninth Annual Research Symposium
Land Disposal, Incineration and
Treatment of Hazardous Waste

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Abstract

This paper presents an overview of the fundamentals of liquid fuel incineration and the results of shock tube experiments investigating the oxidation of pure chlorinated hydrocarbons. In these experiments the ignition behavior of chlorinated methanes, ethanes and benzene were compared with the parent hydrocarbons. The results indicate that it is no more difficult to ignite the chlorinated hydrocarbons which were studied than their analogous hydrocarbons. This appears to be in contradiction with practical experience in incinerators. Preliminary results with spectroscopic measurements of infrared emission from carbon monoxide (CO) and carbon dioxide (CO₂) indicate that the oxidation of CO to CO₂ is inhibited during the combustion of chlorinated hydrocarbons. In the future, these spectroscopic studies will be continued and combined with results from flat flame burner experiments.

INTRODUCTION

Incineration in a properly designed and operated facility has been recommended as a preferred control technology for combustible organic hazardous wastes [22]. In principle, a completely efficient incinerator converts organic hazardous waste material via high temperature thermal oxidation to carbon dioxide (CO₂), water (H₂O), and low volume inert ash material. During the incineration of halogenated hazardous waste streams, significant quantities of the halogen acids will be formed and, if the stream contains dissolved minerals, hazardous salts may be included in particulate

emissions. In order to optimally design incinerators which perform according to current United States Environmental Protection Agency (USEPA) regulations, it is necessary to understand the thermal destruction behavior of organic hazardous wastes. Developing this knowledge is complicated by the fact that there are several different chemical environments present in an incinerator. In each of these regions the rate of conversion of organic wastes into products is controlled by different physical and chemical mechanisms. An appreciation of these differences is also essential for the proper design and modeling of an incinerator.

This paper presents an overview of the fundamentals of liquid fuel incineration and the results of shock tube experiments investigating the oxidation of several pure chlorinated hydrocarbons. In these experiments the ignition behavior of chlorinated methanes, ethanes and benzene were compared with the parent hydrocarbons.

HAZARDOUS WASTE INCINERATION

Overview

A large proportion of organic hazardous wastes occur as liquid streams. The incineration of liquid wastes is an extremely complex process with numerous physical and chemical phenomena involved. The present state-of-the-art does not allow complete characterization of an incineration system nor the a priori prediction of the destruction and removal efficiency (DRE) for a given set of conditions.

A schematic of the subprocesses occurring in a typical turbulent flame, such as that which may be encountered in liquid injection incineration, is shown in Figure 1. The diagram is representative

of phenomena occurring during the combustion of either hazardous wastes or conventional fuels. A number of phenomena including carry over of liquid droplets, vapor carry over due to low temperature, vapor carry over due to unmixedness, inadequate residence time within the flame zone, etc., all may contribute to unsatisfactory system performance.

Generally, the combustion processes in an incinerator may be considered to occur in the following three regimes:

- o Regime 1: Combustion of fuel and oxidizer that have been mixed on a molecular scale. When these reactants are brought to a temperature above the ignition temperature, flame reactions occur and complete and intense combustion is achieved.
- o Regime 2: Thermal reactions of fuel and/or fuel

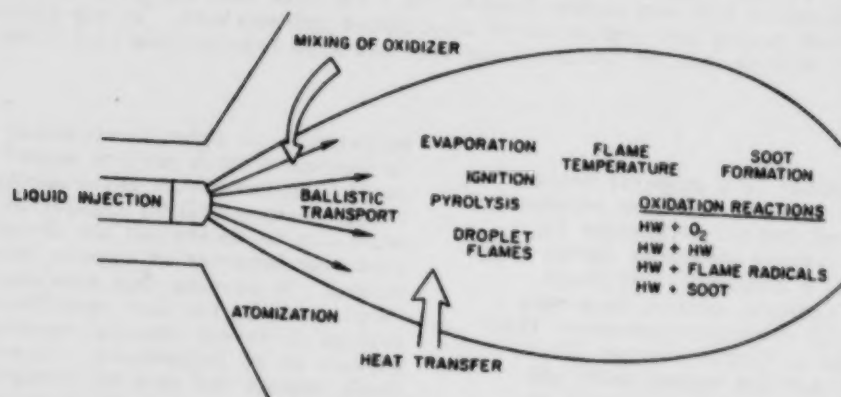


Figure 1. Diagram of the phenomena occurring in a turbulent flame.

fragments in the absence of/or with a limited quantity of oxidizer. This combustion regime occurs within the central core of the flame in a liquid hazardous waste burner. In this regime the fuel is vaporized, pyrolyzed and may result in the formation of soot and other high molecular weight aromatic hydrocarbons or chlorocarbons.

- o Regime 3: Reactions of fuel and/or fuel fragments in the presence of oxidizer at a temperature too low to cause ignition. Complex processes and reactions may occur when some of the liquid fuel is mixed with hot oxidizer and combustion products where the temperature is insufficient to cause ignition.

It is reasonable to expect high destruction efficiencies of hazardous waste compounds that are processed by a flame front. However, waste materials which escape the flame front and are processed in Regimes 2 or 3 are likely not to be adequately destroyed unless the residence times at high temperatures are substantial.

An understanding of the relative time scales associated with the incineration of a pure liquid hazardous waste may be obtained by considering the following sequential processes to occur:

- o Insertion of liquid droplets through a liquid injector into the incinerator
- o Heat transfer between hot gases and the liquid droplet until the droplet reaches its boiling temperature
- o Vaporization of the liquid droplet

- o Mixing of the waste vapor with hot oxidizer
- o Chemical reaction of waste/oxidizer to destroy the waste

Spray Formation

In an incinerator designed to destroy liquid wastes a liquid spray nozzle is generally employed to promote vaporization of the waste by finely atomizing the liquid. This process increases the exposed surface area of the waste by forming droplets having an average size generally in the range of 20-400 micrometer (μm) in diameter.

An understanding of the drop size distribution of organic waste sprays is essential in evaluating the effectiveness of an incinerator system. In particular, it is critical to know the fraction of the total spray that is contained in large diameter droplets. This is due to the fact that the time required to vaporize a droplet is dependent on the square of its diameter. Hence, a drop with a diameter three times greater than the average droplet diameter requires approximately a factor of 10 longer to vaporize than the time required for the average droplet to vaporize.

Generally, liquid spray nozzle manufacturers do not have detailed drop size distribution data. In many cases the only data available is a specification of the Sauter Mean Diameter (d_{sm}) as given below:

$$d_{sm} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (1)$$

where: n_i = number of drops in the spray with diameter d_i (μm). Unfortunately, d_{sm} does not provide information on the distribution of droplet diameters in the spray. Various drop size distribution equations have been developed, but none have been universally accepted [12, 21].

The importance of droplet diameter distribution in a liquid spray can be readily illustrated by considering a simplified hypothetical spray having a

total of 1000 droplets with only three diameters as shown in Table 1. With this hypothetical spray distribution, a Sauter Mean Diameter of 251 μm is calculated. However, the determination of the mass distribution among the three droplet diameter groups is of significance to the incineration process. The mass (m_i) of a droplet with diameter (d_i) is given by:

$$m_i = \frac{\rho \pi d_i^3}{6} \quad (2)$$

where: ρ = the fluid density.
The corresponding mass fraction (MF_i) of the spray contained in each droplet diameter group can be calculated from:

$$MF_i = \frac{m_i n_i}{\sum m_i n_i} \quad (3)$$

Referring to Table 1, 99% of the droplets in this hypothetical spray have a diameter of 100 μm . These droplets, however, represent less than 30% of the total liquid mass associated with the spray. It should also be noted that the large diameter droplets represent only 0.4 percent of the number of droplets but almost 50 percent of the waste mass.

Vaporization

The evaporation and/or combustion of single droplets has received considerable attention. A comprehensive model of these phenomena has not emerged; however, for a wide variety of systems it has been shown that the instantaneous diameter (d) of an evaporating fuel droplet is given by the relation:

$$d^2 = d_o^2 - \lambda_v t \quad (4)$$

where, d_o = initial diameter (millimeters, mm)

t = evaporation time (s)

λ_v = evaporation rate constant (mm²/s).

TABLE 1. WASTE MASS DISTRIBUTION IN A HYPOTHETICAL SPRAY POPULATION OF 1000 DROPLETS

Initial Droplet Diameter, d_o (μm)	Number of Drops, n_i	Initial Mass $MF_i = \frac{m_i n_i}{\sum m_i n_i}$
100	900	0.29
500	6	0.22
750	4	0.49

The time to complete droplet evaporation (t_v) is given by

$$t_v = \frac{d_o^2}{\lambda_v} \quad (5)$$

A number of factors including:

- o ambient temperature
- o liquid physical properties
- o local gas velocity
- o presence of dissolved and suspended solids

affect the numerical value of λ_v . For a wide variety of liquids the numerical value of λ_v in air with a temperature in the range of 1300 K ranges between 0.25 to 2.5 mm²/s. [16].

The evaporation times for various droplet diameters as a function of the evaporation rate constant are summarized in Table 2. Inspection of these results shows that the time required for evaporation may range from 1×10^{-3} s to approximately 4 s. These results clearly indicate that evaporation of large liquid droplets may be an important consideration in determining the destruction efficiency of liquid wastes in incinerators. For example, if the group of droplets having the size distribution of Table 1 is exposed for 0.5 s to an incinerator environment where λ_v is equal to 0.25 mm²/s all of the 100 μm droplets will vaporize.

TABLE 2. EVAPORATION TIME AS A FUNCTION OF INITIAL DROPLET DIAMETER THE EVAPORATION RATE CONSTANT

Initial Diameter, d_0 (μm)	Evaporation Rate Constant, λ_v (mm^2/s)	
	0.25	2.5
50	0.01s	0.001s
100	0.04s	0.004s
500	1.0s	0.1s
750	2.25s	0.225s
1000	4.0s	0.4s

However, applying Equations 2 and 3, the 500 μm and 750 μm droplets will be reduced to 350 μm and 660 μm , respectively. Assuming that the 100 μm diameter family of droplets has vaporized, one can compute the non-vaporized mass fraction of the original spray from the following equation:

$$MF_{ti} = \frac{n_{it} m_{it}}{\sum_i n_i}$$

where MF_{ti} = mass of family i remaining at time t divided by total initial mass

n_{it} = number of non-vaporized droplets in family i at time t

m_{it} = mass of non-vaporized droplets in family i at time t (see eqn. 4)

As shown in Table 3, after 0.5 s in the incinerator environment, 99% of the initial droplets in the spray have been vaporized while 41% of the initial mass remains in the liquid state. From this example it is clear that an incinerator must be designed with consideration for

the larger, less numerous droplets which might be produced during atomization.

Chemical Kinetics

After the liquid wastes have evaporated and mixed with the oxidizer, they must then be destroyed by chemical reactions. Chemical kinetic considerations can be used to determine the rate of chemical reaction. Consider the following elementary chemical reaction:



where A, B, C, D represent chemical compounds, and

a, b, c, d the stoichiometric coefficients.

It has been shown that the rate of reaction of Compound A can be represented by:

$$\frac{1}{a} \frac{d[A]}{dt} = -k(T)[A]^a[B]^b \quad (7)$$

where: $[A]$ = concentration of compound A (moles/cc)

$k(T)$ = chemical rate constant for reaction (6) at temperature T

t = time.

The rate constant, $k(T)$, for a given reaction is conveniently represented in terms of the Arrhenius equation:

$$k(T) = A \exp(-E_a/RT) \quad (8)$$

where: A = frequency factor

E_a = activation energy (cal/gm-mol)

R = universal gas constant (1.98 cal/gm-mole-K)

T = temperature (K).

The rate equations represented by Equations (7) and (8) indicate that the

TABLE 3. MASS DISTRIBUTION IN A HYPOTHETICAL SPRAY AFTER 0.5 s RESIDENCE TIME IN AN INCINERATOR ENVIRONMENT*

Initial Droplet Diameter, d_o (μm)	Initial Number of Drops, n_i	Droplet Diameter After 0.5 s Residence Period, d_t (μm)	Drops Remaining After 0.5 s Residence Period, n_{it}	Mass Remaining After 0.5 s Residence Period, $MF_{ti} = \frac{n_{it}m_{it}}{\sum n_i m_i}$
100	990	0	0	0
500	6	354	6	0.07
750	4	661	4	0.34

*($\lambda_v = 0.25 \text{ mm}^2/\text{s}$)

destruction of a vaporized compound in an incinerator is a function of residence time, species concentrations, and temperature. Since the rate constant, $k(T)$, is exponentially dependent on temperature, the rate of chemical reactions are strongly dependent on the temperature of the incinerator.

In any incinerator system, a host of elementary chemical reactions are occurring simultaneously. It is beyond the scope of this paper to discuss the detailed chemical reactions occurring in an incinerator. However, it is possible to obtain an overview of the time scale of reactions in an incinerator by considering the rate of thermal destruction of a compound (C) which is highly diluted in a constant temperature environment. The rate of reaction of compound C may be approximated by the following pseudo first order kinetic expression:

C $\rightarrow$ products

$$\frac{d[C]}{dt} = -k[C] \quad (9)$$

where: $[C]$ = concentration of the compound at time t

k = rate constant at the reaction temperature

Integrating Equation 9 yields:

$$\ln([C]/[C]_0) = -kt \quad (10)$$

where: $[C]_0$ = the initial concentration of compound A at time $t = 0 \text{ s}$.

Combining Equations (8) and (10) and simplifying yields:

$$[C]/[C]_0 = \exp[-At \exp(-E_a/RT)]$$

Defining the destruction efficiency, DE by:

$$\begin{aligned} DE &= 1 - [C]/[C]_0 \\ &= 1 - \exp[-At \exp(-E_a/RT)] \end{aligned}$$

yields

$$(1 - DE) = \exp[-At \exp(-E_a/RT)] \quad (11)$$

Taking the natural logarithm of both sides of Equation (11) and simplifying yields:

$$t = \exp(E_a/RT) \left[-\frac{\ln(1 - DE)}{A} \right],$$

leading to

$$\ln(t) = E_a/RT + \ln\left[\frac{-\ln(1 - DE)}{A}\right] \quad (12)$$

The use of Equation (12) to determine the time/temperature relationships for a specific first order chemical reaction may best be demonstrated by another example.

In order to effect a 99.99% chemical destruction efficiency, we must set DE in Equation (12) to 0.9999. In many instances the Arrhenius frequency factor (A) for first order decomposition reactions is of the order of 10^{14} s^{-1} [2]. In Figure 2, the $\log_{10} t$ required to destroy a compound to 99.99% DE is shown versus $1/T$ for an A of 10^{14} s^{-1} and a series of overall activation energies. Inspection of these results indicates that the time required to destroy hazardous waste compounds with a DE of 99.99% is strongly dependent on the incinerator temperature and the Arrhenius parameters of the pseudo first order rate constant. Typical parameters for the thermal destruction of a number of dilute organic vapors in air are given in Reference 24.

With these simplifications the time scales for the incineration of liquid hazardous wastes may be approximated. The waste stream is fed to an injector which atomizes the waste into small droplets with a range of sizes that are inserted into an incinerator environment; pressure slightly sub-atmospheric, temperature ~1200K. Heat transfer from the incinerator environment raises the temperature

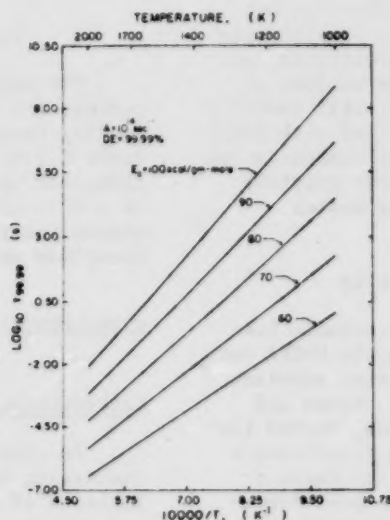


Figure 2. The logarithm of the time required for 99.99% DRE of a compound via a first order decomposition reaction versus temperature.

of the droplet until it reaches its boiling point where it begins to vaporize.

Consider a droplet with an initial diameter of 251 μm , the Sauter Mean diameter of the hypothetical spray of Table 1. The minimum and maximum times for complete vaporization, calculated from Equation 5, are listed in Table 4.

Once in the vapor phase the waste must mix with the oxidizer for combustion to occur. Assuming pseudo first order kinetics, the chemical time required to achieve a DE = 99.99% can be calculated from Equation 12. Table 4 presents these calculations for hazardous wastes within an incinerator operating at 1200K for various values of activation energy, E_a . The time shows a strong dependence on E_a ranging from 0.007 s for $E_a = 60 \text{ kcal/mol}$ to 115,000 s for $E_a = 100 \text{ kcal/mol}$. While the vaporization time of this example is small compared to the chemical kinetic time, droplets with diameters > 251 μm which could contain a majority of the mass in the spray will take significantly longer to vaporize.

This simple example calculation illustrates the importance of basic research on the incineration process, from atomization to chemical kinetics. There are approximations for the time scales of vaporization and chemical kinetics but these depend on information, droplet size distribution and activation energies, not presently available. Approximations of the time scales required for heat transfer and mixing do not exist. Faced with these difficulties the incinerator community has developed measures to rank the relative destructibility of hazardous wastes.

Incinerability Ranking Criteria

In order to incinerate organic hazardous wastes a permit from the USEPA must be obtained. The permit writer examines the components of the waste stream and selects one or more compounds, termed the principal organic hazardous constituents (POHC's). A trial burn of the waste or data in lieu of a trial burn must demonstrate a 99.99 percent destruction and removal efficiency (DRE) of each POHC before a permit is granted. The USEPA guidance manual to permit writers suggests that hazardous waste compounds in the greatest concentration in the waste

stream and waste components which are the most difficult to destroy be designated as POHC's.

In order to select the appropriate POHC's, it is necessary to develop an incinerability ranking scale for hazardous waste compounds. Presently, the USEPA is suggesting the use of the heat of combustion (ΔH_c) as the measure of a compound's incinerability in its guidance manual to permit writers [25].

The choice of ΔH_c as the incinerability ranking parameter has generated controversy in the technical community. Numerous alternative approaches have been suggested to determine the relative incinerability ranking of compounds. These are:

- o Chemical kinetic considerations [24],
- o Autoignition temperature [7],
- o Thermal oxidation and thermal decomposition under non-flame conditions [8, 9],
- o Linear regression models based upon autoignition temperature and structural consideration [18] and
- o Toxicity.

The relative strengths (+) and shortcomings (-) of various incinerability ranking parameters are summarized in Table 5 [10]. Research presently being conducted in this area may ultimately lead to a more effective methodology for determining the relative incinerability of hazardous waste compounds.

EXPERIMENTAL STUDIES

Introduction

In order to develop information concerning the high temperature combustion kinetics of organic hazardous waste compounds, the reaction of selected pure chlorinated hydrocarbons (CHC) and oxygen mixtures when exposed to high temperatures in a shock tube has been investigated. In the operation of a shock tube, a one-

TABLE 4. INCINERATION TIME SCALES

a Complete Vaporization		b Pseudo First Order Kinetics	
$d_0 = 251 \mu\text{m}$ (diam of hypothetical spray)		$DE = 99.99\%$, $A = 10^{14} \text{ s}^{-1}$	
		$T = 1200\text{K}$ (1700F)	
t, s	$\lambda_v, \text{m}^2/\text{s}$	t, s	$E_a, \text{kcal/mol}$
0.26	0.25	0.007	60
0.026	2.5	27.6	80
		115,000	100

TABLE 5. SUMMARY OF STRENGTHS (+) AND SHORTCOMINGS (-) OF PROPOSED INCINERABILITY RANKING PARAMETERS.^a

Parameter	Strengths (+) and Shortcomings (-)
Heat of Combustion Enthalpy change from reactants to products	+ Data available or can be calculated + Relates to heat release and temperature rise - Some apparent inconsistencies in ranking - Correlation with other methods
Autoignition Temperature Temperature at which compound ignites spontaneously in air	+ Correlates with thermal decomposition data + Extensive data available - Value varies with experiment - Some compounds do not autoignite
Chemical Kinetics Reaction path used as measure of incinerability	+ Considers destruction as a rate process + Considers both unimolecular and bimolecular processes - Does not consider physical processes - Limited kinetic data available
Thermal Decomposition Experimental, nonflame determination of destruction efficiency	+ Simple experimental system + Can get 99.99 percent destruction efficiency directly - Does not consider flame reactions - Validity for incineration unknown
Multiple Linear Regression Relates physical and chemical properties to decomposition	+ Considers both AI and structure + Several variables included + Many adjustable parameters + Coefficients obtained from thermal decomposition
Other Methods	+ Heat of formation + Gibbs free energy + Ionization potential + Flash point + Combustion ignition delay + Thermal decomposition in a flame environment

^aSource: Reference [10]

dimensional shock wave is caused to propagate within a tube filled with a potentially reactive gas sample. This shock wave compresses the gas sample, thereby, heating the sample to a temperature high enough to initiate reactions. The progress of the reaction can be monitored in real time by several optical techniques and/or dynamic pressure measurements. In a slightly modified configuration, a gas sample can be heated for a short period of time, then quenched and analyzed later by gas chromatographic or other techniques.

The principle advantages of the shock tube technique are three fold [11, 19].

- 1) Any gas phase compound can be studied; including pure hazardous waste compounds, with or without oxidizer.
- 2) The passage of the shock wave through the experimental gas is equivalent to moving the gas from a reactor at room temperature to another reactor at a specified high temperature in a time on the order of 10^{-10} seconds.
- 3) The typical reaction time in a shock tube (~2 milliseconds) is far shorter than the time for chemical species to diffuse to the walls and hence wall effects are negligible.

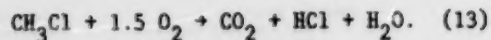
In the initial study, the ignition delay times of selected pure CHC's and oxygen mixtures were measured in the conventional shock tube facility of the Combustion Laboratory of Louisiana State University. Such studies have been useful in determining the combustion characteristics of a wide variety of hydrocarbon fuels [17, 5, 26, 3]. Computer simulations with hydrocarbon oxidation mechanisms proposed in the literature [27] indicate that at the time of ignition the fuel concentration is over 99 percent destroyed. Ignition delay times therefore seemed promising as a measure of compound destruction.

Ignition delay time is defined as the interval between the initial exposure of the CHC oxidizer mixture to a step function change in temperature and the occurrence of the principal exothermicity

of the reaction, which is signified by a sudden increase in temperature and pressure. The duration of this ignition delay time is determined by the overall kinetics of the combustion reactions.

In order to compare the ignition delay times and thereby the combustion mechanisms of selected CHC's with their hydrocarbon analogs, stoichiometric fuel-oxygen mixtures, diluted with argon (Ar), using (1) methane and its chlorinated derivatives, (2) ethane, 1,1,1-trichloroethane, and 1,2-dichloroethane, (3) ethene and trichloroethene, and (4) benzene and monochlorobenzene were shock heated over the temperature ranges listed in Table 6.

When studying hazardous wastes which contain halogen compounds as well as hydrogen and carbon, it is necessary to define a methodology for determining the stoichiometric oxygen or air required for complete combustion of the compound. Incineration temperatures are generally high enough to favor the conversion of almost all of the H and Cl in the hazardous waste to hydrochloric acid (HCl). This indicates that when determining the stoichiometric oxygen requirements for the chlorinated hydrocarbons it should be assumed that maximum conversion of available H and Cl to HCl occurs. Any remaining Cl is assumed to form molecular chlorine (Cl_2) and any remaining H is assumed to form water (H_2O). Based on this reasoning the stoichiometric reaction equation for methyl chloride (CH_3Cl) with O_2 is given by



This definition of stoichiometry was used to determine the test mixture compositions for all the compounds in Table 6.

A useful correlation equation for ignition delay time is of the form [20, 6]:

$$\tau = AT^B \exp(E/RT) [fuel]^a [O_2]^b [Ar]^c \quad (14)$$

where,

τ = ignition delay time (μsec)

T = temperature (K)

R = gas constant (cal/gmmole-K)

[] = concentration (moles/cm³)

A, B, E, a, b, c = empirical constants.

This equation provides a means of comparing shock tube data, but it is not directly applicable to real combustion systems since the O₂ and Ar dependencies must be replaced with an air dependence. A correlation equation of this nature is also derivable from a reaction mechanism [14].

Since many experimental data are required to determine the six empirical constants in Eq. 14 for each fuel of interest, a simpler comparison scheme for ignition delay data was employed in this study [4]. Initial test gas compositions were carefully chosen to allow a direct comparison of the apparent activation energies of the fuels studied without having to explicitly determine the concentration dependencies a, b, and c. In these experiments stoichiometric fuel-oxygen mixtures, diluted in argon, with approximately equal carbon atom concentrations were studied. The pressure behind the reflected shock wave was held nearly constant at 2.0 atm for all experiments. Within these limitations, the measured ignition delay times and the apparent activation energies for the fuels studied may be compared directly.

Experimental Facility

A 76.2 mm diameter stainless steel shock tube was employed (Figure 3) in this study. The ignition delay time was characterized as the interval from the arrival of the shock at the end wall of the tube until the sudden rise in pressure due to the onset of the principle reaction exothermicity as measured by a PCB 113A piezoelectric pressure transducer. The output of the transducer was displayed on a Nicolet Explorer III digital oscilloscope and recorded. Ignition delay times could be read with an accuracy of 5-10%.

Incident shock speeds were measured using piezoelectric pressure transducers to trigger the start and stop channels of interval timers. Transit times between

transducer stations were measured to within $\pm 1 \mu\text{s}$ and the velocity linearly extrapolated to the end wall. The initial temperature and pressure behind the reflected shock wave were computed according to the standard conservation equations assuming no reaction behind the incident shock. Thermodynamic data for enthalpy and specific heat required for the calculations were taken from the JANAF tables [13] and the API Project 44 tables [1] and extrapolated to the 1500-2500 K range.

The liquid chlorocarbons were purified by bulb-to-bulb distillations discarding the first fraction which may contain low-boiling point impurities and the last fraction which may contain high-boiling point impurities. The vapor pressures of the purified liquids were used to prepare the mixtures. The methane, methyl chloride, ethane and ethylene were Matheson CP grade gases and the Ar and O₂ Matheson pre-purified grade gases. The test mixtures were prepared by following standard manometric procedures. Because of the low exothermicity from the oxidation of the chlorinated hydrocarbons it was necessary to use relatively large mole fractions of fuel and oxidizer in order to measure ignition from the pressure traces. The mixtures were stored in stainless steel tanks at approximately 1.1 atm and allowed to mix for a minimum of 36 hours before use.

Results

The natural logarithms of the measured ignition delay times vs. the reciprocal of the initial experimental temperature for the C₁ and both the C₂ and C₆ fuels are plotted in Figs. 4 and 5, respectively. Where possible the data were fit by least squares analysis to an expression of the form

$$\ln \tau = \ln A + (E_a/RT) \quad (15)$$

where

τ = ignition delay time (μs)

R = universal gas constant
(cal/gmmole-K)

T = initial experimental temperature
(K)

TABLE 6. TEST CONDITIONS, FUEL-OXIDIZER MIXTURES, AND LEAST SQUARE PARAMETERS.

Test Mixtures	P (atm)	T Range (K)	ln A (sec)	$E_a/R \times 10^{-3} (K)$
10% CH_4 + 20% O_2 + Ar	2.0	1330-1544	-5.5 ± 1.4	17.6 ± 2.1
10% CH_3Cl + 15% O_2 + Ar	2.0	1280-1570	-3.0 ± 0.7	14.5 ± 3.0
10% CH_2Cl + 10% O_2 + Ar	2.0	1220-1398	-9.0 ± 2.0	19.7 ± 2.9
10% $CHCl_3$ + 10% O_2 + Ar	2.1	1277-1470	----- ^a	----- ^a
10% CCl_4 + 10% O_2 + Ar	2.1	1313-1441	----- ^a	----- ^a
5% C_2H_6 + 17.5% O_2 + Ar	1.7	1155-1287	-7.8 ± 3.7	17.4 ± 4.4
5% 1,2- $C_2H_4Cl_2$ + 12.5% O_2 + Ar	1.8	1188-1540	-6.0 ± 0.4	15.0 ± 0.5
5% 1,1,1- $C_2H_3Cl_3$ + 10% O_2 + Ar	2.3	1288-1618	-0.02 ± 1.2	9.5 ± 1.7
55 C_2H_6 + 15% O_2 + Ar	1.6	1103-1307	-10.4 ± 3.2	19.0 ± 3.6
5% C_2HCl_3 + 10% O_2 + Ar	1.7	1080-1284	----- ^a	----- ^a
1.67% C_6H_6 + 12.5% O_2 + Ar	1.8	1196-1604	-6.7 ± 1.1	16.8 ± 1.2
1.6% C_6H_5Cl + 11.7% O_2 + Ar	1.7	1179-1552	-6.9 ± 0.9	16.6 ± 1.2

^aSee text.

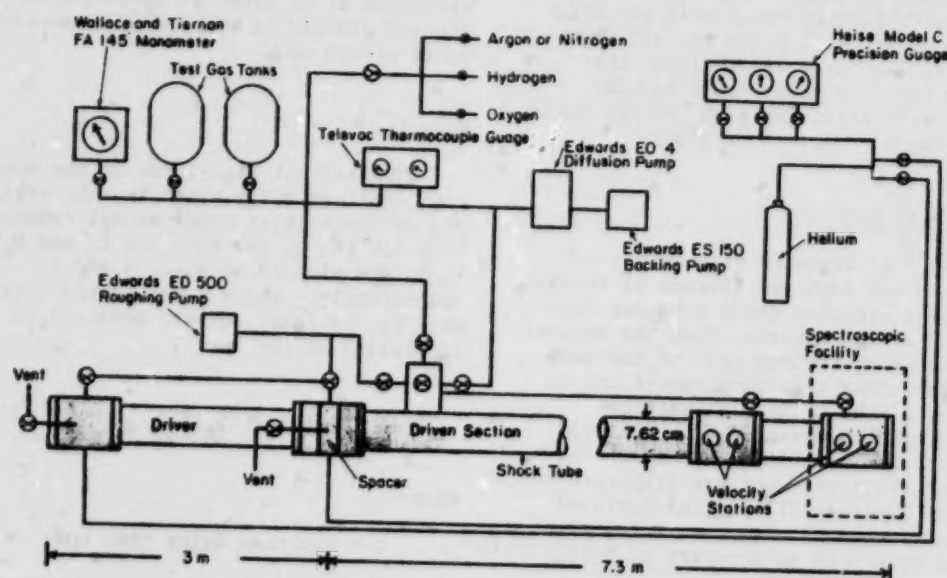


Figure 3. Schematic of the conventional shock tube facility.

A, E_a = empirical constants calculated by least squares.

The least squares lines are also shown in the figures. The reflected shock pressure, the apparent activation energies divided by R (E/R in Eq. 15), fuel/oxidizer compositions, and temperature range for each set of data are shown in Table 6.

Examination of Fig. 4 indicates that CH_4 and CH_2Cl have similar ignition delay times and that dichloromethane (CH_2Cl_2) is more easily ignited. Data for chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) exhibit considerable scatter, but they tend to cluster between the results for CH_4 and CH_2Cl_2 .

Inspection of Fig. 5 indicates that ethylene (C_2H_4) is more readily ignited than any of the C_2 fuels studied. The data for trichloroethene (C_2HCl_3) are too scattered to obtain a good least squares parameters. However, they tend to scatter around the C_2H_4 results. The ignition delays for 1,1,1-trichloroethane ($C_2H_3Cl_3$) are longer than those for ethane (C_2H_6), but the ignition delays of 1,2-dichloroethane ($C_2H_4Cl_2$) are similar to those for C_2H_6 . The measured ignition delays for benzene (C_6H_6) and chlorobenzene (C_6H_5Cl) are nearly identical.

Discussion

The present results seem to indicate that it is no more difficult to ignite the chlorinated hydrocarbons which were studied than their analogous hydrocarbons. This appears to be in contradiction with practical experience in incinerators where it has been reported that chlorinated hydrocarbons are difficult to destroy.

A possible explanation for this difference is that there is a large difference in the "strength" of the ignition between hydrocarbons and progressively more substituted chlorinated hydrocarbons. Once an ignition occurs in the hydrocarbons the reactions are exothermic enough to raise the temperature and completely destroy the fuel; whereas, in contrast the less exothermic CHC ignition may not provide sufficient temperature rise to produce the destruction.

Actually, a comparison of the C-H and C-Cl bond dissociation energies, 415 and 280 kJ/mol, respectively, indicates it is reasonable to expect that the chlorinated compounds will more readily decompose to produce the radical pool required to initiate ignition. This may partially explain the relative ignition delay times of the compounds studied. In addition, recent results obtained near room temperature [15], indicate that the rate of hydroxyl radical (OH) attack on CH_2Cl_2 was faster than OH attack on other chlorinated methanes or on CH_4 .

The conventional explanation of ignition in hydrocarbon oxidation involves the oxidation of carbon monoxide (CO) to carbon dioxide (CO_2) by OH radicals. If this occurs in CHC-oxidation one may ask why is there less exothermicity. In order to examine this important step in the oxidation process, the infrared emission from CO (4.78 μm) and CO_2 (4.25 μm) has been measured for a series of shock tube experiments with 1.5% fuel (CH_4 , CCl_4 and CH_2Cl_2) and stoichiometric oxygen. The analysis of this data indicates that while CO is produced just as readily in the CHC experiments as in CH_4 , CO_2 is not produced. This inhibition of the oxidation of CO to CO_2 during the combustion of CHC's may be an important cause of poor incinerability characteristics of chlorinated hydrocarbons. This hypothesis is in agreement with earlier work which showed that chlorine inhibited carbon monoxide flames [23].

Future Work

The spectroscopic study of the apparent inhibition of the carbon monoxide conversion to carbon dioxide during the oxidation of CHC's is presently continuing in the conventional shock tube of the Louisiana State University Combustion Laboratory. Future directions include the use of a single-pulse shock tube, also in the laboratory at LSU to study the product distributions from the pyrolysis, oxidation and reduction of selected CHC's.

Studies of the behavior of co-fired CHC's will be performed in the flat flame burner facility of LSU's Hazardous Waste Research Center. Initially, the net reaction rate profiles of stable species will be determined during the combustion

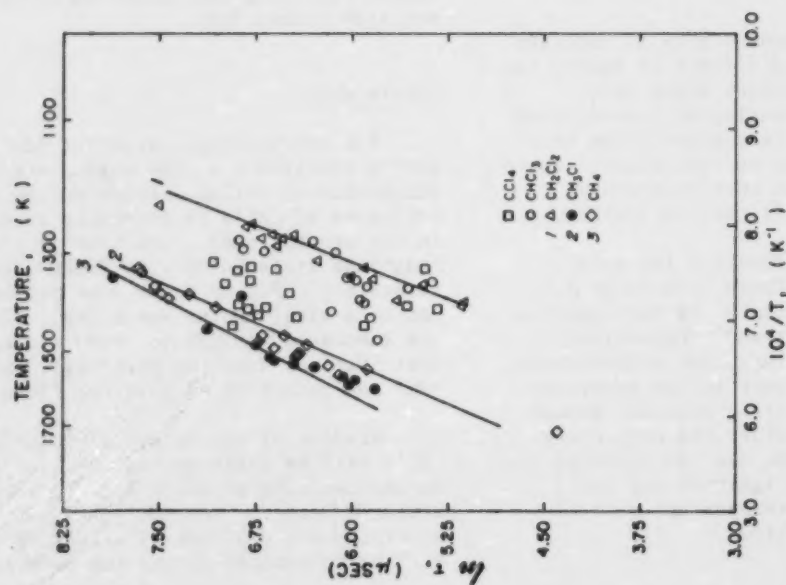


Figure 4. The natural logarithm of ignition delay times versus reciprocal temperature for C_1 hydro and chlorocarbons.

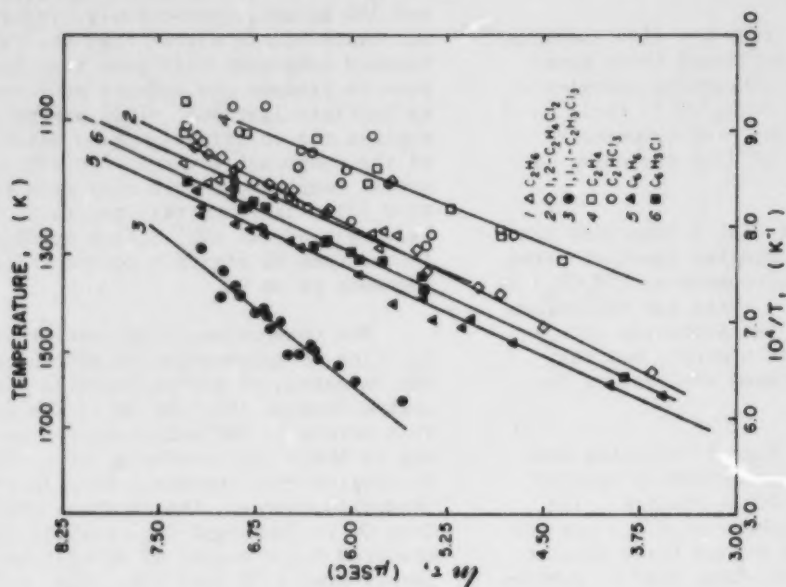


Figure 5. The natural logarithm of ignition delay times versus reciprocal temperature for C_2 and C_6 hydro and chlorocarbons.

process. Similar to the shock tube studies, the overall goal of the flat flame research is to eventually determine the fundamental chemical kinetic reactions which determine the combustion characteristics of chlorinated hydrocarbons.

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This report has been reviewed by the , U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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STATUS REPORT
USEPA COMBUSTION RESEARCH FACILITY
(CRF)

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INTRODUCTION

After extensive planning, designing and a protracted period of budget analysis, the USEPA Combustion Research Facility (CRF) is on the threshold of hazardous waste incineration research. It now becomes extremely important for the EPA and its contractor to conduct research that will be cost effective, useful to the Agency for a better understanding of the complex processes occurring during the incineration of a hazardous waste. Concomitant to those objectives the CRF has the mission to safely conduct experiments using actual industrial waste streams and to develop a system of accurate and precise sampling and monitoring of the process and to initiate an on-site analytical operation that will provide the sophisticated analyses required by legal procedures and citizens acceptance in a reasonable sonable time period.

OBJECTIVES

Principal objectives of the CRF are to carry out pilot scale test burns on hazardous wastes, be they liquid, thixotropic, sludge and/or

solid, that have been previously studied in a laboratory scale system. This will allow the extrapolation of data from the laboratory to pilot scale systems and to indicate differences between idealized laboratory studies and the results from real world equipment. The CRF will constantly strive in all its experimental designs to study the effects, either real or perceived, of important incineration parameters such as residence time, turbulence, temperature, nozzle type and configuration, atomization techniques, etc., on the destruction efficiency of hazardous wastes, and the POHC and PICs associated with the thermal destruction of the waste.

The CRF will provide a vehicle whereby the performance of different design and configuration in commercially available burners and burner types relative to Destruction Efficiency (DE) and other associated incineration operating requirements and/or variables. Ultimately the CRF will provide a mechanism by which the basic performance of different air pollution

control devices can be evaluated in order to permit the intercomparison of apparently comparable devices under a set of standard conditions.

The CRF will establish a detailed test protocol for each incoming waste for study. Early experiments will look at the effects that a variety of operating parameters have on the basic combustion process. Then each parameter will be evaluated as to its contribution to the DE; those found to have minimal effect will be dropped from the test design. Those found to have a major impact will be investigated further. In this way we will be moving toward an understanding of process reliability without process design change. Another aspect of incineration that will play an integral role in the CRF studies is to determine the minimum instrumentation required by an incinerator such that should the process go out of specification appropriate control measures come into action to achieve compliance without a total shutdown occurring. In this regard we will be striving for overall system reliability so that it can be transferred to the field with assurance that it is safe to both man and his environment.

An important aspect of the CRF incinerator lies in the on-line instrumentation that allows the detailed evaluation of the operation of each of the subunits that make up the incinerator. The subunits in question have been defined as the waste, the waste feed and injection system, the kiln, the afterburner and the air pollution control system. The value of this manner of thinking lies in the ability to alter the operating parameters of each subunit in such a way as to introduce non-compliance of the entire system. In essence, such a capability will allow a definition of the critical parameters of each subunit and thereby assist in the

definition of the allowable range of each variable and in the determination of the necessary on-line corrective measures required to assure compliance of the entire system. This approach might be termed "failure mode analysis" (although failure mode analysis is a part of our program, there will be no dangerous emissions to the environment due to a downstream carbon bed/HEPA filter system) of a hazardous waste incinerator.

Integrated throughout the entire CRF operating philosophy is a sound program of health and safety along with system sampling and analysis. All CRF personnel are required to have extensive medical examinations prior to the onset of hazardous waste research. These will be supplemented with annual physical exams and special testing as warranted to specific waste streams. The CRF has, in its basic design, safety of operation, as evidenced by explosion proof glass in the operation room, which will allow visual observation. The wall adjacent to the analytical laboratories has been reinforced with steel and concrete. The roof of the incinerator room has two large ventilation fans so as to prevent combustible gas accumulation and/or dangerous and toxic fume collection.

The CRF has as a vital part of its overall operating mission timely and cost effective analysis of combustion gas for Principal Organic Hazardous Constituents (POHCs) and Products of Incomplete Combustion (PICs) along with residue analysis for hazardous noncombustibles. The laboratories are located on the periphery of the incinerator room and broken into four separate rooms. There is a waste characterization lab where all incoming wastes will be physically characterized prior to incineration. This will insure against incompatible materials going to the incinerator and

will provide insight into material handling requirements and operating parameter boundaries. There are two laboratories concerned with organic chemical analysis from combustion gas before and after scrubber. Here is the heart of the analytical operations and it is in these laboratories that our turn around will be critical to getting the results in a timely fashion. Present thinking dictates evaluation of several analytical procedures for time/cost savings, however, the results must be as accurate and reproducible as established ones or the new procedures will be discarded.

Thus there will be some attempts at analytical methods development all in the direction of speeding up results without losing precision and accuracy. The last laboratory presently has a Thermal Decomposition Unit - Gas Chromatograph (TDU-GC) which will be used to develop basic combustion parameters for each waste while looking for PIC formation. The TDU-GC provides the first basic link in our overall quest for scale-up criteria for process design without getting into a basic design program.

CRF FACTS

1. Construction Cost - \$385,796.52.
2. Physical Dimension - 61' x 51' (see Figures 1 and 2).
3. Operation and Maintenance contract awarded to Versar, Inc. April 1, 1982 for 18 months for a total cost of \$1,417,927.
4. Option 1 for 12 months for \$975,705.
5. Option II for another 12 months for \$1,039,325.

6. CRF personnel on-site, 13 including secretarial and professional staff.

PLANNING TESTING PROGRAMS AND METHODS

The set of experiments to be presented are designed to test the operation and stability of the high temperature zones of the incinerator, the adequacy of the feed system, the air pollution control system, the on-line operation of the control and monitoring systems, and the organic samplers. In addition, the engineering staff will derive hands-on experience with the use of safety equipment and with the effects that such equipment have on the performance of the various activities in and about the incinerator. Finally, these preliminary tests should suffice as a test run on the sample handling, record keeping and laboratory operations prior to the need to deal with more hazardous waste materials, i.e., as an operational test of the QA/QC Program at the CRF.

The results of this series of experiments will be of direct interest to the staff of the CRF in that they will test the procedures and facilities in a live performance. The results will further serve as a basis for judgement of the reliability and utility of future efforts in that the proposed experiments will form a base line for the newly upgraded system against which the effect of future changes can be completed.

Although the explicit details of the proposed experiments will be discussed in more detail below, it is appropriate to discuss the general philosophy of these experiments at this time. Much of the ancillary equipment including the organic samplers as well as the upgraded incinerator still have not been tested under waste feed conditions. These experiments are specifically designed to accomplish this

required testing. In addition, the original equipment manufacturer-supplied air pollution control system (APCS) has been replaced prior to the onset of these experiments. Clearly, the experimental tests will be of value in testing the new APCS. Further, many of the personnel at the CRF have never used safety equipment under any but training activities. The proposed HCB incineration experiments will provide hands-on experience with a substance that is only minimally toxic, but requires, due to its physical properties, minimal safety controls.

As has been pointed out, the EPA incinerator has been provided with the capability of conventional stack sampling under rigorous isokinetic sampling. In addition, facilities have been provided for hot zone sampling in the kiln transfer duct and within the afterburner output duct.

Sampling at the stack will utilize EPA Methods 1 and 2 for the determination of the gas flow parameters. Sampling for residual HCB will be conducted using standard EPA Method 5 with toluene as the stripping solution. Upon completion of the sampling run, the entire sampling train will be transferred to the laboratory for sample extraction and train clean up.

To estimate the duration of sampling it is only necessary to note that, with a feed rate of 100 gm/hr and a DRE of 99.99 percent, the emission rate (q_0) should approximately be:

$$q_0 = 1 \cdot 10^{-2} \text{ gm/hr}$$

The flue gas generation rate is approximately 400 SCFM so that the residual HCB concentration, C_0 , in the flue

gases would be:

$$C_0 = 4.17 \times 10^{-7} \text{ gm/SCF}$$

If this stream is sampled at the rate of 10 l/min for one hour, then a total mass, M_0 , of HCB would be collected, where:

$$\begin{aligned} M_0 &= \frac{600}{28.34} \times 4.17 \times 10^{-7} \\ &= 8.8 \times 10^{-6} \text{ gms} \end{aligned}$$

Introducing the assumption that reduction of the extract to 10 ml and the subsequent injection of 5 ul into the GC would result in an absolute mass, M^* , injected of:

$$\begin{aligned} M^* &= 8.83 \times 10^{-7} \times 5 \times 10^{-3} \\ &= 4.415 \times 10^{-9} \text{ gms} \end{aligned}$$

Since the absolute sensitivity of the electron capture detector is said to be of the order of 1×10^{-9} gm (actual laboratory data from the CRF suggests that the actual detection level is at least an order of magnitude lower than this estimate), clearly the sample taken for 1 hour is more than adequate for the detection of a DRE of 99.99 percent. Hence, stack sampling will require a 1 hour sampling period.

In addition to sampling for the POHC (in this case, HCB) in the stack as well as in both the kiln transfer line and in the afterburner exit line, a number of additional parameters will be sampled. The listing of these parameters, the method by which monitoring will be accomplished and the details of monitoring appears as Table 1 for stack measurements. Tables 2 and 3 provide the same information for sampling rates at the kiln transfer line and afterburner exit duct, respectively.

A number of additional miscellaneous parameters will be monitored during the test burns. These are listed in Tables 4 and 5.

EXPERIMENTAL DESIGN

It is the explicit purpose of this set of experiments to test the newly completed upgrading of the CRF incinerator and its ancillary equipment. For this reason, a rather extensive series of tests has been proposed. It will first be essential to test the liquid and pressure integrity of the Andersen 2000 APC equipment which will be carried out using neutral water so as to minimize possible cleanup problems should leaks be detected. It is further required that the effectiveness of the demister be determined (as will be discussed below, the effectiveness of the demister will determine the significance of future stack testing at the CRF). Finally, the overall system must be tested including the Bendix analyzer, the organic samplers, the feed system and the control and monitoring systems. This latter series of tests will be carried out using HCB as the test material. It is estimated that a series of light experiments will be required to ascertain the necessary information on the detailed operation of the system and of its components. The detailed measurements that will be taken are indicated in Table 6 which follows the justification of each of the experiments.

EXPERIMENT 1

The Andersen system has been just been installed and therefore requires that the integrity of the many piping junctions be tested. Since there is the possibility that leaks will be detected it is desired that testing be accomplished with water rather than

with the caustic solution. In addition to the testing of the integrity of the piping it is also of interest to determine the effectiveness of the demister which will be accomplished by a stack determination of aerosol water. Finally, both the temperature and the ambient pressure will be determined at the important points throughout the system. It is anticipated that this experiment will require a full day for its completion.

EXPERIMENT 2

In experiment 2, the Andersen will be operated at pH 9 in order to test the adequacy of the pH control system, the use of caustic in the absence of HCl, the residual solids concentration in the blowdown, the effect of caustic on the CO₂ concentration in the stack gases and a further test of the demister through a determination of the Na concentration in the stack gases. This experiment is also expected to require a full day of testing.

The accepted method for the determination of HCl emission require the collection of the HCl in an aqueous medium followed by quantitation using a chloride ion specific electrode. Clearly, NaCl is going to be produced within the scrubber and, if there is significant carry over of NaCl particles, the resulting Cl ion concentration in the stack sample will give erroneous estimates of the HCl emission. Clearly, the presence of sodium in a stack sample, as in experiment 2 can only result from particulate carry over which indicates inadequate operation of the demister.

EXPERIMENT 3

In experiment 3 further exercising of the general system will be accomplished. In addition, the ability of the feed system to feed the 1:1

water/glycerine solution at a rate of 1 gal/hr will be determined. This experiment should be completed in 4 hours.

EXPERIMENT 4

As in experiment 3, all system will be subjected to additional testing with the feed system operating at near its maximum rate of 10 gal/hr. This experiment should require approximately 3 hours for completion.

It should be noted that the first four experiments will also be used to determine the possibility of contaminants being introduced into the organic samplers from the sample lines due to extraction by the hot gases. In the next members of the proposed set of experiments, the system will be challenged using HCB as the POHC.

EXPERIMENT 5

This experiment has as its goals the challenging of the system and its ability to achieve the required DRE of 99.99 percent for HCB. In addition, the kiln temperature has been selected so that there should be very little decomposition of the HCB therein. This has been introduced in order to determine the efficiency of the heated sample lines to prevent the condensation of HCB prior to the impingers. It is further designed to determine the efficiency of the Andersen system to deal with low concentrations of HCl in the flue gases.

EXPERIMENT 6

This experiment has the same general goals as experiment 5 with a ten-fold increase in HCB concentration and the corresponding ten-fold increase in HCl concentration.

EXPERIMENT 7

This experiment has, as its goal, a determination of the effect of kiln temperature on the overall DRE of the system for a compound such as HCB.

EXPERIMENT 8

Experiment 8 is designed to determine the effect of AB exit temperature on the DRE attainable by the system. Further, since lowering the AB exit temperature results in lowering the flue gas flow rate (in ACFM), this experiment will also test the effect of a reduced input flow rate on the scrubber efficiency for the removal of HCl.

ANTICIPATED RESULTS

This set of experiments has been designed for the purpose of testing all facets of the newly upgraded incinerator. The results of these experiments should serve to establish a base line on the operation of each of the basic elements of the present system and to establish the normal operating characteristics of these elements.

STATUS

The CRF has in-place an approved Quality Assurance/Quality Control project description, project responsibility, QA objectives, sampling/measurement, sample identification and custody, calibration procedures and frequency, analytical methods, data reduction, validation and reporting, internal quality control checks, performance and system audits, preventive maintenance, routine procedures used to assess data precision, accuracy and completeness, corrective action and quality assurance reports to management. This document can be obtained by requesting a copy from the EPA.

The Health and Safety Manual is an integral part of all CRF activities and has been in place since September 1982. This manual is broken into the following components: administrative requirements, general facility safety rules and guidelines, CRF respiratory protection program, medical surveillance program, health and safety training program, facility security, personal protective equipment, safety equipment, mechanical and electrical equipment and compressed gases, emergency responses, response to fire emergencies, chemical spills, response to loss of electricity or water, waste transport, handling and testing, and storage, use and disposal of laboratory chemicals. This manual is available upon request also from the USEPA.

A document entitled "Utilization of the USEPA Combustion Research Facility" has been prepared that describes in detail much of the facility and its operating philosophy. At the present time, it is being reviewed and updated and is not publically available.

FUTURE

By mid-Spring of 1983, physical start-up activities at the CRF should be in complete action. Immediately following the start-up the action plans call for a test burn using the HCB test plan as previously described. Following this, the rotary kiln system will be subjected to a POHC "soup" for system and analytical testing. During this period of time a complete RCRA Part A and B hazardous waste facility permit application will be developed and formally submitted to Arkansas authorities for their approval. It is anticipated that during this RCRA permit application procedure a special short term permit will be requested in order to permit actual

hazardous waste research activities to continue.

Recent decisions by EPA officials have resulted in the design plans for fabrication and shakedown of a research pilot-scale liquid injection incinerator to accompany the present rotary kiln system. When complete the CRF will possess the capability to conduct hazardous waste research on technology that presently covers about 90 percent of all field capability. This will surely make the CRF and its accompanying TDU-GC and analytical laboratories one of the most comprehensive research facilities for this particular activity in the world.

Anticipated benefits from CRF activities cover such operating parameters as mixing, residence time distribution effects, refractory type and thickness, injection/atomization techniques, feed rate, parameter control systems and concepts such as operation conformance to predetermined operating conditions. The CRF will constantly strive to develop simplified analytical procedures so as to reduce the cost burden of test burns and shorten the turnaround time from burn to results. We are looking to developing in-line combustion as sampling and analysis for controlling basic operating parameter.

Since operations have begun at the CRF it has been determined that the facility qualifies as a major RCRA facility and must submit a formal Part A and B facility permit application. This will entail a significant effort on behalf of the Versar Senior staff and the on-site EPA project officer. Also since we are in an R&D mode of operation, the tests must be conducted in an upset mode. Therefore, it has been determined that down stream of the normal stack emission, there will be a carbon bed/HEPA filter system to insure

there are no toxic or hazardous emissions to the environment. This was not in the original plans for the CRF but has been included as operations can truly study hazardous waste incineration and develop operating conditions based on less than optimal conditions studied at CRF. Studying incineration at upset conditions is novel and will assist the regulators significantly in establishing standard operating conditions for field units and should provide insight for scale-up criteria to design engineers studying scaling of incinerator systems.

A PROFILE OF EXISTING HAZARDOUS WASTE INCINERATION FACILITIES

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Abstract

The incineration of hazardous wastes has been receiving increasing attention since the implementation of the Resource Conservation and Recovery Act of 1976 (RCRA). The MITRE Corporation is under contract to the U.S. Environmental Protection Agency (EPA) to assist in the development of a hazardous waste incineration (HWI) data management system. A major part of this effort centers on the verification which began in late 1981 and is still underway, a profile of hazardous waste incineration in the United States has been developed.

The principal approach was to follow-up and verify data extracted from the RCRA Part A applications submitted to EPA by facilities who indicated incineration as one of their process codes. Information was obtained from 514 of the 566 such facilities listed in the EPA's automated Hazardous Waste Data Management System on 30 November 1981 plus 23 facilities identified outside the data base. Facility spokesmen were asked to verify the existence of hazardous waste incinerators at their facilities, design characteristics, operational parameters and the types and quantities of hazardous waste incinerated.

This paper summarizes the results of the study. A total of 284 operational hazardous waste incinerators were verified at 219 facilities. Projection of these figures for the entire population results in an estimate of approximately 350 operational incinerators at 270 facilities.

Other data presented include geographical location of facilities, types and capacities of incinerators, combustion zone temperatures and residence times, types and quantities of wastes burned, and the use of heat recovery and air pollution control devices.

INTRODUCTION

The U.S. Environmental Protection Agency (4) (EPA) estimates that 57 million tons of organic hazardous wastes are generated annually in the United States. Current estimates indicate that perhaps 40 to 50 percent of this waste can be disposed of by using thermal destruction technologies. EPA regards incineration as a principal technology candidate for destroying hazardous waste. Since the Congress enacted the Resource Conservation and Recovery Act of 1976 (RCRA), incineration has been included among those hazardous waste disposal technologies that are regulated by the Agency.

In 1980, the U.S. EPA (3) promulgated regulations requiring every facility which is treating, storing or disposing of hazardous waste to file Part A of the RCRA permit application form. The data submitted on these forms was stored in a computer information system entitled "Hazardous Waste Data Management System" (HWDMS) which is operated in each of the 10 EPA Regions. The Incineration Research Branch of EPA's Industrial Environmental Research Laboratory in Cincinnati has expanded HWDMS and is developing the Hazardous Waste Control Technology Data Base (HWCTDB) to manage detailed incineration engineering data, trial burn data and related information.

The information presented in this paper is based on part of the data assembled for the HWCTDB project. The topics to be discussed include a profile of existing incinerator facilities and a profile of incinerator manufacturers.

PROFILE OF EXISTING INCINERATION FACILITIES

The existing facilities data discussed in this paper were assembled originally in support of the Regulatory Impact Analysis Program for proposed regulations concerning hazardous waste incineration (Keitz et al. 2). The approach to the data assembly began with preparation of a list of all known facilities which might have one or more operational hazardous waste incinerators. As of the 30 November 1981 cutoff date established for this list, 612 such facilities were identified. The HWDMS contained 566 of these and 46 were identified from other sources. However, at that time it was known that some of the Part A applications had not yet been entered into HWDMS. Based on later information obtained from HWDMS in July 1982 (estimated 100% complete), it was calculated that the list of 612 facilities was approximately 90 percent complete.

Initial telephone contacts with many of these facilities showed that a significant number did not have an operational hazardous waste incinerator. Of the 612 facilities, a total of 537 facility spokesmen indicated whether or not their facility had an operational hazardous waste incinerator and provided varying amounts of additional information. The summary findings discussed here are based on the information verified by these 537 facilities.

Table 1 shows the hazardous waste incineration status of these 537 facilities divided into EPA regions. A total of 284 operational HW incinerators were identified at 219 facilities. Thus only 40.8% of

TABLE 1
STATUS OF HAZARDOUS WASTE INCINERATION FACILITIES IN EACH EPA REGION^a

Region	Operational Facilities	Operational Incinerators	Facilities With No Operational Incinerators	Under Construction	Status Unknown	Sample Size
I	10	12	34	3	1	48
II	22	28	46	4	1	73
III	23	30	48	5	0	76
IV	46	59	52	6 ^b	0	102
V	29	31	44	3	0	76
VI	62	95	28	4 ^b	0	93
VII	8	8	11	3	0	22
VIII	5	5	9	1	1	16
IX	14	16	14	3	0	31
X	0	0	0	0	0	0
TOTAL	219	284	286	32 ^b	3	537

^aInformation obtained from an estimated 81% of the HWI facility population.

^bThree facilities have both an operational unit and a unit under construction; two in Region IV and one in Region VI.

the facilities contacted verified having an operational HW incinerator. Inspection of the list of facilities in the HWDMS data base in July 1982 showed that there were 128 facilities not previously contacted during the telephone campaign. If it is assumed that these facilities have the same verification rate as those contacted earlier, then an additional 52 facilities should have 68 operational HW incinerators. It is therefore estimated that there are approximately 350 operational HW incinerators at 270 facilities in the United States.

Table 2 shows the number of operational HW incinerators by type. Of the 264 incinerators whose type was specified, 208 (79 percent) are capable of burning liquids by injection. Twenty-nine units (11 percent) are capable of burning bulk wastes (solids or liquids). The remaining types are mostly special purpose units such as steel drum reconditioning burners or military ammunition disposal units.

Table 3 shows the design capacities of operational HW incinerators. Design capacities were reported for 180 incinerators burning liquids and 44 incinerators burning solids. The median design capacity of incinerators burning liquids is 150 gallons per hour with most units (86 percent) not exceeding 1000 gallons per hour. Incinerators burning solids tend to have smaller capacities with the median being approximately 650 pounds per hour (equivalent to 78 gallons of water per hour).

Table 4 shows the temperature and gaseous residence time for operational HW incinerators. Gaseous residence times were reported for 104 incinerators. The median

combustion temperature was approximately 1800°F (980°C), and median gaseous residence time was slightly under 2 seconds. It should be noted, however, that residence times can be calculated by many techniques and the respondents were not asked to indicate the technique. Therefore, care should be exercised in interpreting this data.

Table 5 shows the major wastes burned and the number of facilities reporting these wastes. Most of the wastes reported are liquids, principally spent non-halogenated solvents and aqueous solutions of corrosives, reactives or ignitables. About 600,000 tons per year of wastes were actually weak aqueous solutions containing only a few percent of the hazardous substance reported. These solutions accounted for 59 percent by weight of all wastes reported. The most frequently reported waste was the non-listed ignitable waste with high heat content (less than 6000 Btu per pound). This waste was reported for 69 incinerators. The largest single category of waste by weight was non-halogenated solvents (EPA Code F003) accounting for 223,000 tons per year at 18 incinerators.

PROFILE OF THE HAZARDOUS WASTE INCINERATOR MANUFACTURING INDUSTRY

During February and March 1981, incinerator manufacturers were contacted in order to determine those marketing hazardous waste units (Frankel et al., 1). Four directories were used to provide names, addresses and telephone numbers of manufacturers, specifically:

TABLE 2 TYPE AND NUMBER OF OPERATIONAL HW INCINERATORS^a

Type	Number	Percent of Total Specified
Liquid Injection	136	51
Hearth with Liquid Injection	33	12
Fume with Liquid Injection	24	9
Rotary Kiln with Liquid Injection	10	4
Combination System ^b	5	2
Rotary Kiln (Solids Only)	1	1
Hearth (Solids Only)	23	9
Ammunition and Explosives	12	5
Drum Burner	7	3
Other ^c	<u>13</u>	<u>5</u>
Total Specified	264	100
Total Not Specified	<u>20</u>	
TOTAL	284	

^aInformation obtained from an estimated 81% of the HWI facility population.

^bIncludes interconnected multiple units (e.g., rotary kiln in series with liquid injection unit).

^cIncludes such items as fluidized bed incinerators.

TABLE 3
DESIGN CAPACITY OF OPERATIONAL HAZARDOUS WASTE INCINERATORS^a

Incinerators Burning Liquids			Incinerators Burning Solids		
Capacity (Gallons/Hour)	Number of Incinerators	Percent of Total Specified	Capacity (Pounds/Hour)	Number of Incinerators	Percent of Total Specified
0 - 50	48	27	0 - 100	4	9
51 - 100	28	16	101 - 300	5	11
101 - 200	22	12	301 - 500	7	16
201 - 300	22	12	501 - 1000	12	27
301 - 500	12	7	1001 - 2000	6	14
501 - 1000	23	13	2001 - 5000	7	16
1001 - 2000	17	9	5001 - 10,000	1	2
2001 - 10,000	8	4	10,001 - 20,000	2	5
Total Specified	180	100	Total specified	44	100
Unspecified	28		Unspecified	17	
TOTAL	208		TOTAL	61	

^aInformation obtained from an estimated 81% of the HWI facility population.

TABLE 4
REPORTED MAXIMUM TEMPERATURE AND GASEOUS RESIDENCE TIME
FOR OPERATIONAL HAZARDOUS WASTE INCINERATORS^a

Residence Time (seconds)	Maximum Temperature				Not Specified	Total
	1600°F	1600°F -1900°F	1901°F -2200°F	2200°F		
<1.0	7	2	0	4	1	14
1.0 - 1.9	8	17	6	5	4	40
>2.0	8	3	32	7	0	50
Not Specified	<u>13</u>	<u>42</u>	<u>12</u>	<u>7</u>	<u>106</u>	<u>180</u>
TOTAL	36	64	50	23	111	284

^aInformation obtained from an estimated 81% of the HWI facility population.

TABLE 5
NUMBER OF HW INCINERATORS REPORTING MAJOR WASTES AND QUANTITY BURNED^a

EPA Waste Code	Description	Number of Incinerators Reporting			Quantity Short Tons/Year
		Waste	Quantity		
D001	Ignitables (High Btu, High HW) ^b	69	60		39,578
D001	Ignitables (Low Btu, Low HW) ^b	19	17		140,015
D001	Ignitables (High Btu, Low HW) ^b	6	3		5,870
D001	Ignitables (Waste Light Oils)	3	2		1,610
D001	Ignitables (Unspecified)	7	5		21,190
D002, D003	Corrosives and Reactives	32	30		191,895
F001, F002	Spent Halogenated Solvents	18	11		17,945
F003	Spent Non-Halogenated Solvents	22	18		233,120
F005	Spent Non-Halogenated Solvents	24	21		18,253
K011	Acrylonitrile Production Bottoms	3	3		120,000
K016-K020	Hvy Ends, Cl Chemical Production	10	10		38,165
K049	Slop Oil Solids, Petroleum Ref.	1	1		5,000
P063	Discarded Hydrocyanic Acid	6	5		135,325
U220	Discarded Toluene	3	3		10,801

^a Information obtained from an estimated 81% of the HWI facility population.

^b High Btu = 6000 Btu per pound.

High HW = major portion of waste is hazardous (e.g., organic liquids).

Low HW = major portion of waste is non-hazardous (e.g., contaminated water).

- 1981 Chemical Engineering Catalog
- February 1981 Buyer's Guide, Pollution Equipment News
- 1981 Catalog and Buyer's Guide, Pollution Equipment News
- 1980-81 Directory and Resource Book, Air Pollution Control Association

Hazardous waste incinerator manufacturers were asked to voluntarily provide information about the types of incinerators manufactured, the approximate number of units sold between 1969 and 1981, and design and operating information. 1969 was selected as a cutoff date based upon several manufacturers' estimates that 12 years of useful service may be expected from a hazardous waste incinerator. A summary of the number of manufacturing companies and the number of incinerators in service classified by type is presented in Table 6.

Liquid injection incinerators are most prevalent with 64.0 percent of the market, hearth incinerators comprise 20.8 percent of the units sold, and 12.3 percent of the incinerators are rotary kilns. These three types account for 97 percent of the units manufactured.

Of the 57 companies identified as marketing hazardous waste incinerators, 28 have sold no units in the United States. Apparently many of the companies that have not sold an incinerator are anticipating a large market growth. Of the 23 companies marketing liquid injection incinerators, eight have sold none to date; eight of the 17 companies offering rotary kiln incinerators

have sold none to date; and five of the nine companies offering fluidized bed incinerators have sold none to date. All hearth incinerator manufacturers have sold at least one unit. Most of the companies offering innovative incineration technology have not sold any units to date.

Incinerator capacities may be related by the thermal input or the mass input to the combustion chambers. The ranges and typical values of the capacities of the major types of incinerators are presented in Table 7. Hearth incinerators generally have the smallest capacity of the major types, although rotary hearths can be constructed with capabilities up to 170 million Btu/hr. Typical rotary kiln and liquid injection incinerators have approximately the same capacity. Although the largest incinerator listed in Table 7 has a capacity of 150 million Btu/hr, some manufacturers have received requests to bid on facilities as large as 300 Btu/hr.

COMPARISON OF OPERATIONAL DATA WITH MANUFACTURERS' DATA

Table 8 presents a comparison of the number of HW incinerators reported by manufacturers and existing HW facilities. A total of 284 operational HW incinerators were identified at 219 facilities. If a projection of these facility figures is made to account for the estimated 128 facilities from which data were not obtained, the total operational HW incinerator population would be approximately 350 at 270 facilities. This figure agrees very well with the 335 operational units reported by manufacturers. In contrast,

TABLE 6. NUMBER OF HAZARDOUS WASTE INCINERATORS SOLD IN THE UNITED STATES.

Type of Incinerator	Number of Manufacturing Companies	Hazardous Waste Incinerators Sold	Percent of Total
Liquid Injection	23	219	64.0
Fixed Hearth	12	59	17.3
Rotary Kiln	17	42 ^{a,b}	12.3
Fluidized Bed	9	9	2.6
Multiple Chamber Hearth	2	7	2.0
Pulse Hearth	1	2	0.6
Rotary Health	1	2 ^c	0.6
Salt Bath	2	0	—
Induction Heating	1	0	—
Reciprocating Grate	1	1	0.3
Infrared Heating	1	1 ^c	0.3
Open Drum	1	0	—
Total		342	100.0

^aIncludes five units in construction.

^bIncludes one oscillating kiln.

^cIncludes one unit in construction.

TABLE 7
DESIGN CAPACITIES OF HAZARDOUS WASTE INCINERATOR TYPES
(From Manufacturers' Data)

Incinerator Type	Mass Capacity		Thermal Capacity	
	Range lb/hr	Statistical Value and Population	Typical Value lb/hr	Statistical Value and Population
Liquid Injection	30 - 24,500	Median of 43	1,600	Range 10 ⁶ Btu/hr 0.125 - 130
Hearth	25 - 2,500	Average of 48	810	Median of 50
Rotary Kiln	1200 - 2080	Average of 2	1,600	Average of 4
Fluidized Bed	---	1 Only	31,000	Median of 34
				Average of 5
				Typical Value 10 ⁶ Btu/hr
				8
				4.9
				10.3
				45.5

TABLE 8. COMPARISON OF NUMBER OF HAZARDOUS WASTE INCINERATORS
REPORTED BY MANUFACTURERS AND HWI FACILITIES

	Reported by HWI Facilities Contacted		Reported by Manufacturers
	Actual Number Reported	Projection for Total Population	
Operational Incinerators	284	350	335
Units Under Construction	32	40	7
Total Reported	316	390	342

existing facilities reported 32 units under construction which is much higher than the 7 reported by the manufacturers.

Table 9 presents a comparison of the types of operational HW incinerators reported by manufacturers and HW facilities. The manufacturer's data and the projected total existing population agree extremely well for the liquid injection and hearth type incinerators. However, the rotary kiln population reported by manufacturers is more than double the number reported by facilities. Reasons for the discrepancies may include: some of the units sold since 1969 may no longer be in use or may now burn non-hazardous wastes; some manufacturers might not have been given enough information to know whether the customer's wastes are hazardous; or, some manufacturers may not know if the customer's wastes are regulated under RCRA or the Toxic Substances Control Act. All of these may cause high or low estimates of the number of incinerators.

SUMMARY

This paper has presented a brief look at hazardous waste incineration from two views: namely, existing facilities, and the incinerator manufacturing industry. A large majority of the wastes incinerated are liquids with aqueous solutions predominating. A wide variety of incinerators were shown to be in operation throughout the nation with reasonable agreement between data reported by operational facilities and the incinerator manufacturing industry. In addition, the data tends to substantiate some concepts which heretofore were mostly assumptions. These include the locations, types and capacities

of hazardous waste incinerators. On the other hand, some concepts previously assumed will require modification. Among these are the total number of facilities incinerating hazardous waste and the nature of the wastes incinerated. In many cases the decision to operate a hazardous waste incinerator appears to have been selected only when other choices such as material recovery, recycling, energy recovery or other disposal methods were not cost-effective.

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TABLE 9. COMPARISON OF THE TYPES OF OPERATIONAL HW INCINERATORS
REPORTED BY MANUFACTURERS AND HWI FACILITIES

	Reported by HWI Facilities Contacted		Reported by Manufacturers
	Actual Number Reported	Projection for Total Population	
Liquid Injection	159(a)	213	219
Hearth	56(b)	75	70
Rotary Kiln	13(b,c)	17	37
Fluidized Bed	4	5	9
Other	31(d)	42	(e)
Type not Specified	<u>20</u>	<u>0</u>	<u>(e)</u>
Total Operational	284	352	335

- (a) = includes fume/liquid units.
 (b) = includes units both with and without liquid injection.
 (c) = includes 2 rotary kilns in combination units.
 (d) = includes 3 combination units not having a rotary kiln.
 (e) = this category not obtained from manufacturers.

PARTICULATE AND HCl EMISSIONS FROM HAZARDOUS WASTE INCINERATORS

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ABSTRACT

EPA regulations place limits on particulate and HCl emissions from hazardous waste incinerators. MRI has collected particulate and HCl emissions data from a variety of such incinerators. This paper evaluates the data, control system performance, and probable mechanisms and relationships affecting emissions. Results indicate that alkaline scrubbing and particulate emissions may be related.

INTRODUCTION

EPA regulations (under RCRA) for hazardous waste incinerators require that particulate emissions be no more than 180 mg/Nm^3 (0.08 gr/dscf) corrected to 7% O_2 , and that chloride removal efficiency be no less than 99% if chloride emissions exceed 1.8 kg/h (4 lb/h). As a result, most hazardous waste incinerators which handle waste containing chlorinated compounds are equipped with particulate/HCl removal systems. This equipment usually involves some type of wet scrubbing device, the most common being packed towers, venturi scrubbers, or electrified scrubbers. In some cases the scrubbing medium is water only; but in other cases, the scrubbers utilize recirculated water with the addition of alkaline materials (caustic or lime) to neutralize absorbed HCl.

This paper emphasizes HCl and particulate emissions, and factors related to the control of these emissions. Data and results discussed in the paper are primarily based on recent work done for EPA by Midwest Research Institute (MRI).

The next section summarizes how these emissions are determined and the implications of the measurement methods which may not be immediately obvious.

MEASUREMENTS OF HCl AND PARTICULATE EMISSIONS

The EPA Modified Method 5 sampling train, as shown in Figure 1, is used to collect samples for particulate and chloride emission measurements. The probe, cyclone, and filter are the only components used to quantify particulate emissions, and the only components used to quantify chloride emissions are the contents of the condensate and KOH impingers.

The probe cyclone and filter components are maintained at a temperature of $121^\circ \pm 14^\circ\text{C}$ ($250^\circ \pm 25^\circ\text{F}$) during sampling. Therefore, any droplets carried over from the scrubber would be evaporated after they entered the sampling probe. If those droplets contained dissolved HCl, not combined

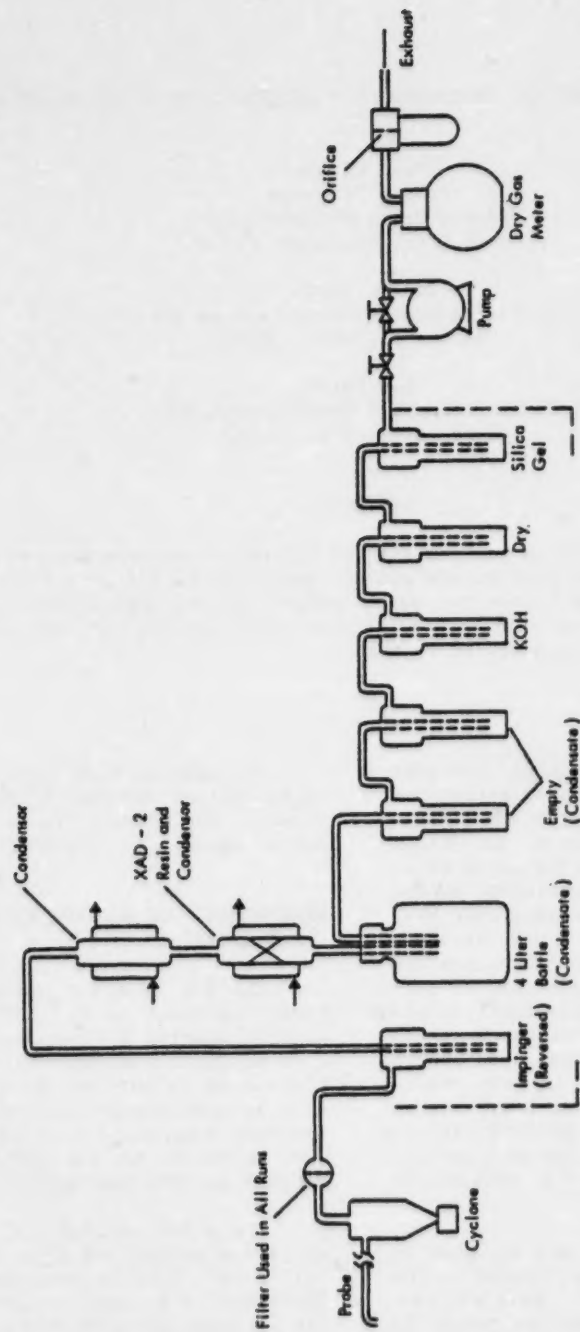


Figure 1. Schematic Illustration of Sampling Train

with any alkali salts, then the HCl would be returned to the gaseous state and would pass through the filter and be captured by the condensate or KOH and quantified as part of the chloride emissions. On the other hand, if the droplets contained suspended or dissolved solids (e.g., NaCl or CaCl_2), these could form particulate matter when the droplets evaporated, which should be captured on the filter and quantified as part of the particulate emissions. As a result, droplet carryover may increase either the chloride or the particulate emissions, or both, depending on the composition of the droplets. This aspect of the sampling method is pertinent to the discussion of HCl and particulate emission data presented in subsequent sections.

HCl EMISSIONS

During the combustion process, HCl emissions are formed from chlorine compounds in incinerator waste feeds. It is the function of scrubbing systems to absorb this gaseous HCl from the combustion gases and to achieve 99% removal, the requirement under RCRA (unless emissions are below 1.8 kg/h).

MRI has tested several hazardous waste incinerators burning high Cl wastes that utilize some type of wet scrubbing system. Data for six of these facilities are given in Table 1 and show that at least five of the six achieved the required 99% HCl removal. The first facility listed in Table 1 (Plant A) achieved 99% efficiency when operating normally with caustic addition to maintain the scrubbing liquid at pH 4, but HCl removal was below 99% when the pH of the scrubbing liquid was quite low (pH 1).

It would appear from the data in Table 1 that Plant B achieved 99% HCl removal even though the pH of the liquid effluent was low (pH 2). However, the pH of this effluent was raised to a much higher value (~ pH 10) by addition of lime, after which the solution was recirculated back to the scrubbers. Thus, the pH of the liquid fed to the scrubbers was about pH 10 even though the outlet liquid had a low pH of about 2.

An HCl removal efficiency of 99% was achieved by three plants that used water only with no alkaline addition to the scrubbing liquid. Two of these (Plants E and F) used once-through water, which means that water usage was relatively large. The other plant (Plant D) utilized water recirculation but incorporated three packed towers in series, with the fresh makeup water being fed to the top of the third tower. Liquid effluent from this third tower was then fed to the second tower, and so on.

Based on the data presented, it is clear that 99% HCl removal can be achieved by wet scrubbing systems without necessarily using alkaline scrubbing solutions. In fact, theoretical calculations of HCl removal efficiency, as outlined in Bonner et al. (1), have been carried out by MRI using average design and operating characteristics for scrubbers employed at hazardous waste incinerators. These theoretical calculations, based on a normal water makeup and drawoff rate of the recirculating liquid, have shown that 99% HCl removal is achievable using water only. However, in water-only systems, the pH of the liquid would be low, and this acidity must be taken into account in selecting construction materials.

On the basis of the theoretical calculations, one might question why Plant A did not achieve 99% removal even when the caustic addition system malfunctioned, resulting in a scrubbing liquid with low pH. MRI testing was done during the period without the mist eliminator, so, based on the particulate emission data, it is believed that there was excessive carryover of scrubbing liquid. Any HCl dissolved in droplets carried over from the scrubber would cause an increase in the measured HCl emissions.

For systems with alkali addition, any droplet carryover of the scrubbing solution could result in an increase in the measured particulate emissions instead of an increase in the HCl emissions. Alkaline additives and/or soluble reaction products (NaCl or CaCl_2), as well as any suspended solids, can adversely affect the measured particulate emissions, especially if the

TABLE 1. SUMMARY OF DATA ON PARTICULATE CONCENTRATION AND HCl REMOVAL EFFICIENCY FOR INCINERATORS BURNING WASTES CONTAINING CHLORINATED COMPOUNDS

Plant	Scrubbing system	Alkaline scrubbing media	Mist eliminator	Avg HCl removal efficiency and pH of scrubber effluent	Avg particulate emissions mg/Nm ³ (gr/dscf) at 7% O ₂
A	75-cm water column (w.c.) ΔP venturi → sieve tray tower	Caustic	See last column	> 99% at pH 4; < 99% at pH 1	1,520 (0.666) (no mist eliminator) 220 (0.095) (with mist eliminator)
B	Packed tower → 1-stage electrified scrubber (ES)	Lime	Yes	> 99% at pH 2	78 (0.034)
C	Packed tower → packed tower → 2-stage ES	Caustic	Yes	> 99% at pH 5	150 (0.066)
D	300 cm w.c. ΔP venturi → 3 packed towers in series	H ₂ O only	Yes	> 99%*	23 (0.010)
E	1 packed tower	Once-through H ₂ O	Yes	> 99% at pH 1	200 (0.088)
F	1 packed tower	Once-through H ₂ O	Yes	> 99% at pH 1.5	4 (0.002)

* pH of final effluent was 2 but is not comparable to other systems since this plant used three scrubbers in series with feed-forward water flow.

system is not equipped with a good mist eliminator. This subject is discussed in the following section.

PARTICULATE EMISSIONS

Achieving the particulate emission limit of 180 mg/Nm^3 (0.08 gr/dscf), corrected to 7% O_2 , may be more difficult than achieving 99% HCl removal. The level of particulate emissions is influenced by several factors that are represented by the equation:

$$\text{Particulate emissions} = (A + Q)(1 - \text{Eff}) + C$$

- where:
- A = Amount of ash in waste feed that becomes suspended in combustion gases
 - Q = Solids produced by quenching with recirculated scrubbing solution
 - Eff = Particulate removal efficiency of control system
 - C = Particulate resulting from droplet carryover

Important aspects of each of the factors in the above equation are discussed in the following paragraphs.

Combustion

All wastes contain some "ash," the amount of which can vary widely. Solid waste usually has the highest ash content. During the combustion process, a portion of this ash is suspended in the combustion gases, which is the origin of some of the particulate matter that must be removed to achieve a stack concentration of 180 mg/Nm^3 (0.08 gr/dscf).

None of the tests conducted by MRI involved determination of the particulate concentration in the very hot combustion gases prior to quenching or scrubbing. However, if an incinerator burned a liquid waste containing 4% ash and, if all the ash entered the combustion gas stream, the resultant particulate concentration in the combustion gases would be about $2,000 \text{ mg/Nm}^3$ (1 gr/dscf).

Quenching

Quenching cools the hot combustion gases before they enter the particulate/HCl control system. Water sprayed into the gas stream to achieve this cooling effect may also achieve some particulate control. The amount sprayed into the hot gas stream usually exceeds the amount evaporated in the quenching process; thus, some particulate may be removed by impaction with water droplets. In some plants, however, part of the recirculated solution from the scrubbers is used for quenching. Some of the water droplets sprayed into the quenching section will be totally evaporated and any solids dissolved in those droplets would become part of the particulate that enters into, and must be removed by, the control system.

Control Systems

The type and configuration of control systems installed for particulate/HCl removal vary widely from plant to plant. They may involve use of a venturi scrubber followed by one or more packed towers, or packed towers only. Two plants tested by MRI also used electrified scrubbers (ES). Basically, these devices consist of a high voltage section for charging the particles in the gas stream. These charged particles are then collected by a series of grounded vertical plates with a continuous flow of liquid down the surface of the plates.

Some of the variations in control system configuration are shown schematically in Figure 2. The systems also vary in operation. For example, the venturi scrubber at one plant was designed to operate at a pressure drop of 70 to 100 cm water column (w.c.) (30 to 40 in. w.c.) while one at another plant operated as high as 300 cm w.c. (120 in. w.c.). All of the plants tested by MRI used at least one packed tower, except for Plant A, which used a sieve tray tower. The packed towers or tray towers are primarily intended for HCl removal and characteristically have low pressure drops of 10 to 25 cm w.c. (5 to 10 in. of H_2O). Packed towers may provide some particulate removal, but low pressure drop systems of this type have poor particulate removal efficiency for small particles ($< 5 \mu\text{m}$). Only one of the tests conducted by MRI included determination of particle size at the inlet to the

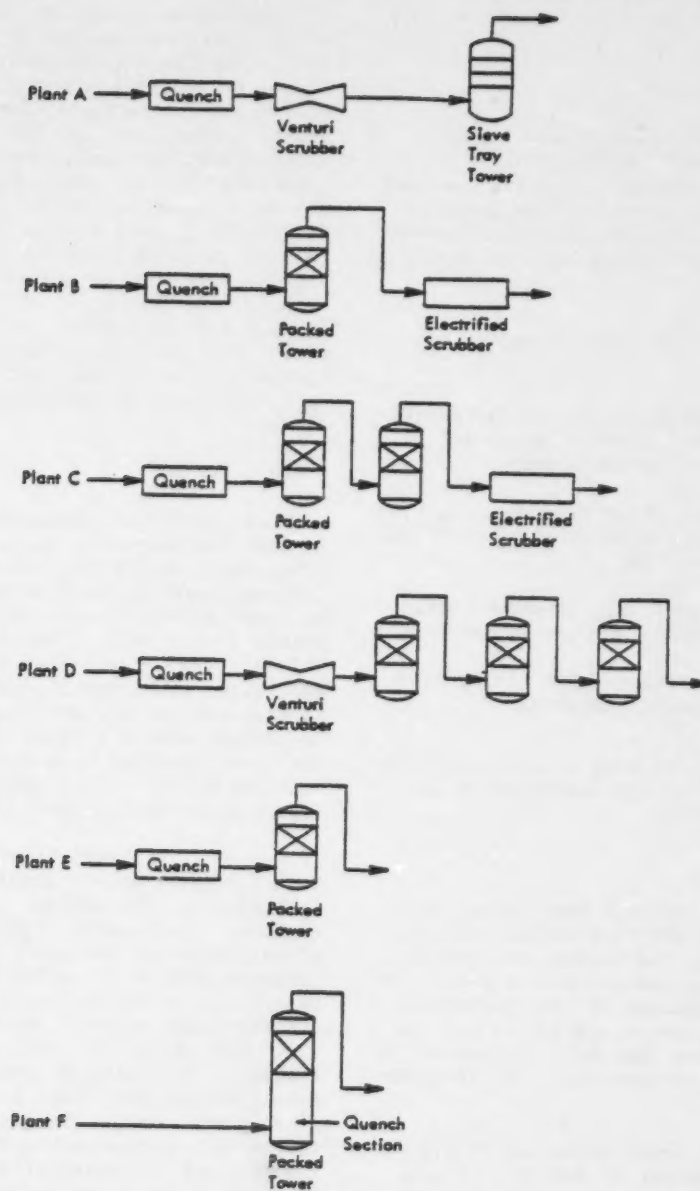


Figure 2. Schematic Diagram of Control Systems at Various Plants

particulate removal system (after quenching). This test showed that at least 90% of the particulate (by weight) was less than $2\text{ }\mu\text{m}$ in size. This strongly suggests that unless the waste feed had low ash content, packed towers alone could not achieve the particulate limit of 180 mg/Nm^3 (0.08 gr/dscf) and that other control devices (e.g., venturi scrubbers or ES) are necessary for that purpose.

It is possible that, no matter how efficient such particulate removal devices are, the particulate limit may be exceeded. If a particulate removal device is followed by a packed tower (for HCl removal), droplets carried over from the packed tower could contain dissolved salts which would adversely affect particulate test results (as discussed in "HCl Emissions" section). For this reason most of the plants listed in Table 1 were equipped with mist eliminators. Tests at Plant A showed the dramatic difference between operating with and without a mist eliminator, and suggest that a mist eliminator can reduce particulate concentrations by more than $1,200\text{ mg/Nm}^3$.

One caution, however, is that information in Maroti (2) states that the quoted amount of carryover from mist eliminators, ranging from 40 to 400 mg/m^3 (0.02 to 0.2 gr/acf), is much lower than limited field and laboratory data indicate (400 to $4,000\text{ mg/m}^3$). If droplet carryover were as high as $4,000\text{ mg/m}^3$ (2.0 gr/acf) and the droplets contained only 1% dissolved salts, the resultant particulate concentration would be 50 mg/m^3 (0.02 gr/acf), representing at least one-fourth of the allowable limit of 180 mg/Nm^3 (0.08 gr/dscf).

Discussion of Data

Particulate emission data presented in Table 1 for the six incinerators studied show that four facilities met the particulate limit of 180 mg/Nm^3 (0.08 gr/dscf) corrected to 7% O_2 , while two did not. The data for Plant A clearly demonstrated a drastic reduction in particulate emissions after the mist eliminator was installed, but emissions were still slightly above the limit of 180 mg/Nm^3 (0.08 gr/dscf). It is not known whether this was due to inadequate performance of the venturi scrubber or the need for even better mist eliminators.

Plant E is the other of the two plants which exceeded the particulate limit. Considering that Plant E was equipped with only a packed tower, it is not too surprising that it did not meet the particulate limit. It is somewhat surprising, however, that the emissions were close to the limit. The liquid waste fed to this incinerator was from an associated chemical operation, so it may have been low in ash content. Similarly, it is believed that the waste feed for plant F was low in ash content.

Based on the above findings, it is evident that, unless the waste feed is very low in ash content, some type of particulate removal device is needed at hazardous waste incinerators in order to achieve the limit of 180 mg/Nm^3 (0.08 gr/dscf) and that packed towers alone are probably not adequate for meeting that goal. It is not possible from the data at hand to ascertain exactly what the particulate removal system must be for incinerators burning wastes with high ash content, although data from Plant A indicate that a 70-cm (30-in.) ΔP venturi may not be sufficient. This is not inconsistent with control device performance, considering the very small particle size of $90\% < 2\text{ }\mu\text{m}$. The data also indicate that incinerators burning low ash content wastes may achieve the limit without any particulate removal device.

It is apparent from the data that packed towers require installation of effective mist eliminators. It had been postulated that the need for effective mist eliminators would be more critical for plants using alkaline scrubbing for HCl removal, since any carryover of this solution would adversely impact particulate emissions. In an effort to investigate this aspect, available data were compiled on metals content of the emitted particulate for Plants B, C, and D. Plants B and C used recirculated alkaline scrubbing solution while Plant D used water only. The available data on the metals detected in the particulate (by acid digestion and ICAP analysis) are shown in Table 2. Both Plants B and C indicated significantly higher Na concentrations than did Plant D. In Plant C the higher Na concentration is presumably related to the use of caustic scrubbing. Although Plant B used lime scrubbing, there is reason to believe that the lime slurry contained a relatively high

TABLE 2. COMPARISON OF METALS CONTAINED IN STACK PARTICULATE (%)

	Plant B* Runs 6, 7, 8	Plant C Runs 1-3	Plant D Run 2
Al	0.1	0.2	ND
Ca	0.9	0.8	ND
Fe	1.5	0.2	4.8
K	1.8	0.4	ND
Na	15.3	18.6	6.4
Pb	4.8	8.4	1.9

ND = Not detected.

* Analysis of particulate collected in tests prior to plant modifications which reduced the particulate emissions.

concentration of Na. The results for Plant B do not show higher Ca content, however, as might be expected for lime scrubbing. Insufficient data are available to explain this inconsistency.

It should be noted in Table 2 that the total of the major metals detected for each plant is on the order of 20 to 30% of the total particulate. But these data represent only elements, not compounds. Thus, if the particulate contained 15% Na, then the equivalent percentage of NaCl would be 38%, which is a significant portion of the total particulate.

The MRI tests also included analyzing for metals in the waste feeds. The particulate and waste feed data were then used to calculate the output rate of each metal (g/min) in the particulate emissions and the input rate of each metal in the waste feeds. The data were expressed as the percentage of input that was emitted from the stack as particulate (Table 3). Thus, the higher the number, the greater the portion emitted (i.e., 100% would indicate that the amount emitted equals the input amount).

Data in Table 3 reflect differences from plant to plant in particulate removal efficiency. For Plants B and C, the data show a relatively large percentage of Na being emitted in comparison to other metals (Al, Ca, Fe). What is even more evident in

TABLE 3. PERCENTAGE OF MASS INPUT FOR EACH METAL THAT IS EMITTED AS PARTICULATE

	Output rate as percent of input rate (%)		
	Plant B	Plant C	Plant D
Al	1.6	0.6	ND
Ca	4.1	3.9	ND
Fe	9.7	1.1	0.7
K	120	16	ND
Na	49	15	0.7
Pb	5.9	17	1.1

ND = Not detected in particulate samples.

Table 3 is that a large percentage of the K was being emitted. One possible explanation for these findings is that the Na and K emissions include contribution of those two very soluble components from carryover of alkaline scrubbing liquids used in Plants B and C. Apparently substantiating this fact is that at Plant D, which did not use alkaline scrubbing, there are no large differences in the percentage of each metal emitted.

CONCLUSION

MRI's analysis of information and data obtained in tests at six hazardous waste incinerators was used to assess HCl removal and particulate emissions. The data show that 99% HCl removal efficiency was achieved at five of six plants, and was also achieved at the sixth plant (Plant A) when it was operating normally. Three of the plants that achieved 99% efficiency used water only, which shows that alkaline scrubbing is not necessarily required to achieve 99% HCl removal efficiency.

Two of the six plants tested did not achieve the particulate emission limit of 180 mg/Nm³ (0.08 gr/dscf), corrected to 7% O₂. One of these used only a packed tower. The other used a 70-cm (30-in.) ΔP venturi scrubber. Considering the probable small size of the particulate (as determined at one plant), there is reason to believe that the particulate limit will not be easy to achieve.

Particulate control devices better than a 70-cm ΔP venturi may be necessary, except in those situations where the waste feed has a low ash content. Another important aspect of meeting the particulate limit is that effective mist eliminators must be used in conjunction with packed towers or other alkaline scrubbing devices. Available data on metals analysis of particulate emissions indicate that carryover of soluble alkali metals (Na, K) from alkaline scrubbing systems may represent a significant portion of the particulate emissions.

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EMISSION TEST RESULTS FOR A HAZARDOUS WASTE INCINERATION RIA

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ABSTRACT

The Environmental Protection Agency is preparing a Regulatory Impact Analysis (RIA) of hazardous waste incineration. Data from 20 tests were gathered for this analysis including tests conducted by Midwest Research Institute (MRI) at eight incinerators. The scope of MRI's test program is described and the results are summarized. The test covered a range of waste and incinerator types, combustion temperatures, and residence times. Principal organic hazardous constituents (POHC) were identified and quantified in the waste feeds and stack effluents to determine destruction and removal efficiencies (DRE). A number of products of incomplete combustion (PIC) were also identified and quantified in the stack effluent. Other measurements made were POHC in liquid and solid effluents; chlorides and metals in all effluents; and particulate, hydrocarbon, and carbon monoxide in the stack effluent.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) has resulted in the Environmental Protection Agency (EPA) enacting hazardous waste regulations affecting all who generate, store, transport, treat, and dispose of such wastes. While several disposal and treatment options are available, incineration has received a great deal of attention because it is a technology that is presently available and provides permanent disposal of many organic wastes. As part of EPA's program, the Office of Solid Waste (OSW) is required under Executive Order 12291 to conduct a Regulatory Impact Analysis (RIA) to ascertain the costs and benefits associated with various approaches to regulating hazardous waste incinerators. Integral parts of this process are the definition of current performance, and

evaluation of the effect of various incinerator design and operating parameters on the destruction of hazardous organic pollutants and the effectiveness of control devices for the removal of particulate and HCl emissions. EPA's Office of Research and Development (ORD) is also actively pursuing the advancement of knowledge about hazardous waste incineration by providing technical support to OSW and looking at longer range research needs.

Over the last year MRI has conducted tests at hazardous waste incinerators to provide data for EPA's programs. The tests were similar to incinerator trial burns, but had a broader scope. A wide variety of samples were collected at eight incineration facilities.

Table 1 summarizes the types of samples collected and the analyses performed. Emphasis was on measurement of principal organic hazardous constituents (POHCs), products of incomplete combustion (PICs), chlorides, and particulates. Samples of all input and effluent streams were collected at every site and archived after specified analyses were performed.

Composite samples of the wastes and grab samples of liquid and ash effluents were collected. Stack sampling methods included a Modified EPA Method 5 for particulates, semivolatile POHCs and PICs, and chlorides; two methods for collecting volatile POHCs and PICs, an integrated gas bag and the volatile organic sampling train (VOST); and continuous gas analyzers for O_2 , CO, CO_2 , and total hydrocarbons. Analyses of POHCs and PICs were by gas chromatography/mass spectrometry (GC/MS), and metals were analyzed by inductively coupled argon plasma (ICAP) or atomic absorption (AA). Details on the sampling and analysis methods used were presented by Dr. Gregory A. Jungclaus in an earlier paper at this conference.

This paper is an overview of MRI's testing results. It characterizes the incinerator sites and wastes that were

burned and summarizes the results of the tests. Specific characteristics or results are not presented for each site separately due to confidentiality agreements with some of the sites tested.

SITE CHARACTERIZATION

The eight incinerators tested are characterized by a wide variety of incinerator types, waste types, and operating conditions. Table 2 shows the distribution of incinerator types and control devices. All eight incinerators had liquid injection burners. Four injected both aqueous and organic liquid wastes. Five of them had a rotary kiln or hearth for solids (two did not feed solids during the test), and one ducted gaseous waste directly to the incinerator. Three of the incinerators did not have any air pollutant control devices. The other five had packed scrubbers for HCl control, and four of those five also had a particulate control device.

The eight facilities can be further classified as on-site and off-site, four of each. On-site facilities are those located at the waste generation site that dispose of wastes from a single firm or process.

TABLE 1. SAMPLING AND ANALYSIS OF INCINERATORS

Samples collected	Analyses performed at all sites	Analyses performed at selected sites
Waste feed	POHCs Chloride Heating value Water	Metals Ash Viscosity
Stack gas	POHCs/PICs Chloride Particulate Continuous monitoring (O_2 , CO_2 , CO, HC)	Metals
Scrubber liquid		POHCs Chloride Metals
Ash		POHCs Chloride Metals

TABLE 2. DISTRIBUTION OF INCINERATOR TYPES AND CONTROL DEVICES

Incinerator type	Number of facilities
Liquid injection	8
Rotary kiln	2
Hearth	3
Gas injection	1
Control device	Number of facilities
None	3
HCl scrubber	5
Particulate control	4

Off-site facilities are commercial disposers that handle wastes from a large number of sources. Figure 1 shows the distribution of capacities for each of these classes. The on-site facilities ranged in capacity from 50 to 1,400 kg/h (100 to 3,000 lb/h) of waste feed or 1 to 33 GJ/h (1 to 31 million Btu/h). The off-site facilities ranged from 600 to 6,000 kg/h (1,300 to 13,000 lb/h) or 9 to 78 GJ/h (9 to 74 million Btu/h). Besides having higher capacities, off-site facilities generally incinerated a much greater variety of wastes. Solid and aqueous liquid wastes were more frequently handled at off-site facilities, and both the physical state and chemical composition of the wastes were much more varied than at on-site facilities.

WASTE CHARACTERIZATION

Overall, three of the eight facilities handled only organic liquid waste; two handled organic and aqueous liquid waste; and the remaining three handled organic and aqueous liquids and drummed solid wastes.

Figure 2 shows the variation in some waste characteristics by type of waste. The heating values were below 4,600 kJ/kg (2,000 Btu/lb) for aqueous liquids, and ranged from 14,000 to 37,000 kJ/kg (6,000 to 16,000 Btu/lb) for organic liquids and from 7,000 to 23,000 kJ/kg (3,000 to 10,000 Btu/lb) for solid wastes. The organic liquids and many of the solids had a high enough heating value to sustain

combustion without auxiliary fuel. Percent chloride in the wastes ranged up to 25%, with the highest values occurring for organic liquids (chlorinated solvents). Little ash was found in aqueous liquids; in organic liquids values ranged up to 9%; and solids had the most ash with values around 17%. Obviously, water content is high for the aqueous wastes, but it also ranged up to 50 to 60% for the organic liquids and solids.

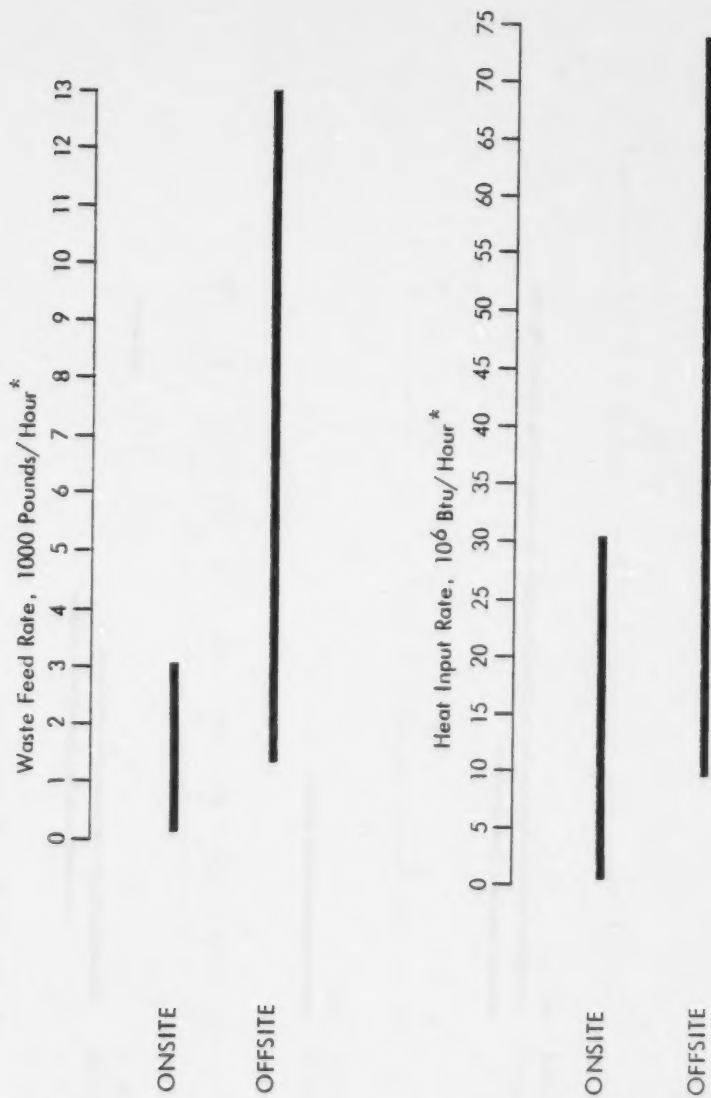
COMBUSTION PARAMETER CHARACTERIZATION

Values for design and operating parameters varied widely from facility to facility. Every facility had unique design or operating features. Multiple combustion chambers were common, some with separate waste feeds. Example arrangements were parallel chambers (e.g., a kiln for solid wastes and a separate liquid injection unit) or primary and secondary chambers in series.

Table 3 shows the range of values for three key parameters: combustion temperature, residence time, and percent excess air or percent oxygen. Temperatures ranged from 820° to 1100°C (1500° to 2100°F). The values presented are those recorded on each facility's instruments. They represent a fair picture of the range of values; however, when comparing values from site to site it is important to consider the location of the thermocouple because the temperature reading can vary several hundred degrees depending on its location. Residence times varied from 0.2 to 6.5 s. Again, the range is representative, but individual values are difficult to interpret. Values were calculated from combustion chamber volumes and average flow rates. At times a section of the stack or duct contained gases at high temperature and might legitimately have been considered part of the combustion volume. At facilities with multiple chambers at different temperatures it could be difficult to select the proper time/temperature to consider. As Table 3 shows, excess air values fell within a range of 60 to 130% and corresponding oxygen content ranged from 8 to 12%.

ORGANIC EMISSIONS

From this varied population of incinerators with different designs and



* 1 pound/hour = 2.2 kilograms/hour; 10^6 Btu/hour = 0.95 GigaJoules/hour

Figure 1. Distribution of Incineration Capacities

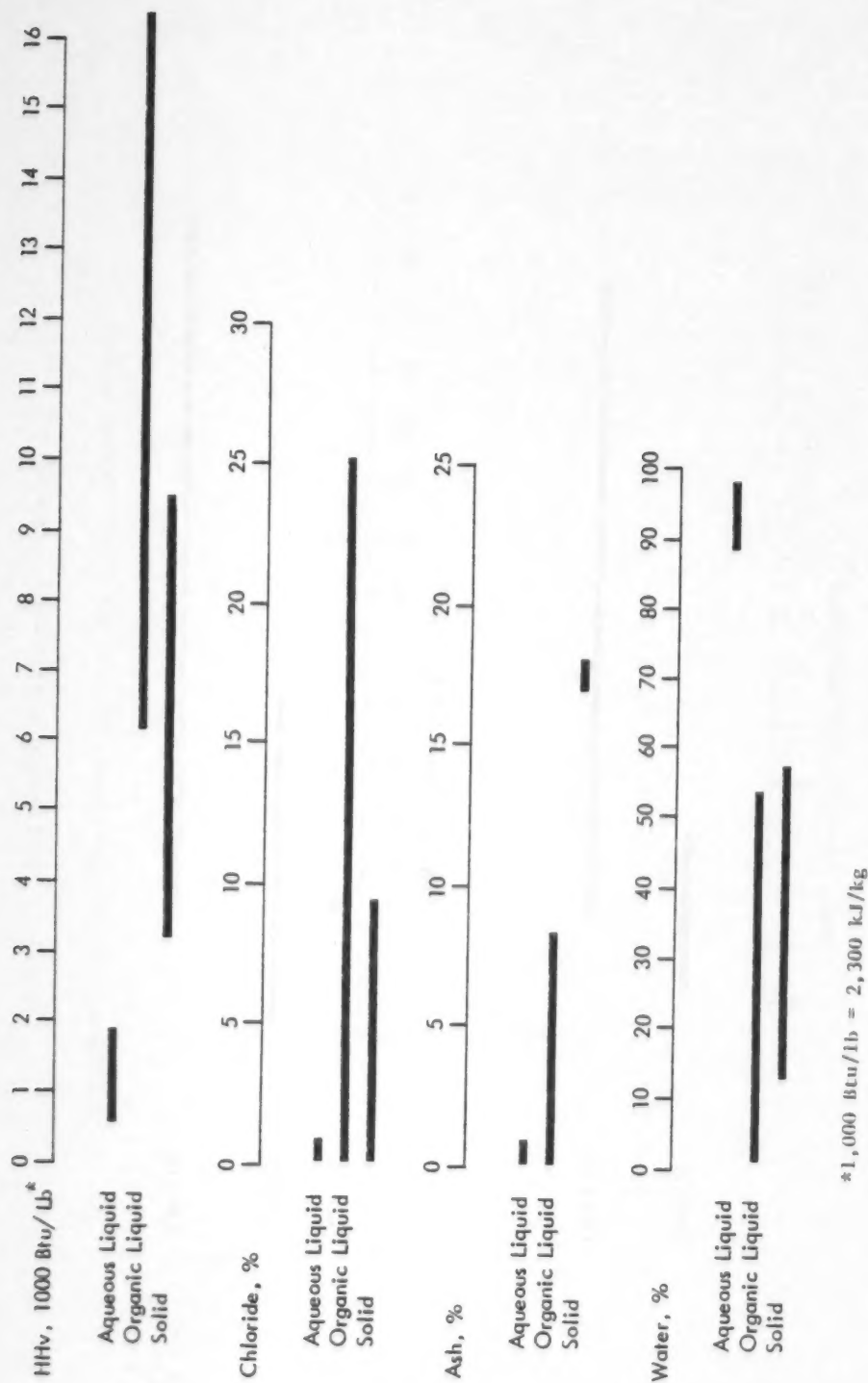


Figure 2. Waste Characterization

TABLE 3. SELECTED PROCESS PARAMETERS

Temperature, °C (°F)	820-1100 (1500-2075)
Residence time, s	0.2-6.5
Excess air, %	60-130
Oxygen, %	8-12

operating conditions, a large number of data points were gathered for many compounds. Samples were analyzed for all Appendix VIII compounds. Table 4 shows a list of the POHCs most often identified and the frequency with which each compound was found in the 22 waste streams burned for all facilities. This table lists compounds contained on EPA's list of POHCs that were found at 100 ppm or greater concentrations in a given waste. They frequency of occurrence of carbon tetrachloride (CCl₄) and trichloroethylene (TCE) are artificially high because these compounds were spiked into the waste at most sites. Excluding these two compounds, the most frequently encountered POHCs were toluene and tetrachloroethylene. Twenty-one other POHCs were found in one waste stream each.

Destruction and removal efficiencies (DREs) were calculated for all POHCs identified in the wastes at each site. Figure 3 displays the overall range of DREs measured for all compounds and for a few specific compounds where data were available for several sites. Each data point represents a test average for one POHC. The results span a wide range of DREs, though about 35% of the data points fall between 99.99 and 99.999% DRE. Another 20% are just below 99.99% DRE. As with the entire data set, the results for specific compounds also cover a wide range.

The lowest DREs shown in Figure 3 tended to occur when one or both of two factors were present. First, there is a trend in the data that indicates lower DREs will result when POHC concentrations in the waste are low; below 1,000 ppm. This might reflect deviation from the common assumption that combustion of POHCs is a first order reaction, since DRE does not vary with input concentration for a first order reaction. Second, lower DREs tended to occur for POHCs that were identified as

TABLE 4. POHCs FOUND IN WASTE STREAMS*

POHC	Number of waste streams
Toluene	17
Tetrachloroethylene	10
Trichloroethylene	10
Carbon tetrachloride	8
Naphthalene	7
Chloroform	6
Methylene chloride	6
Methyl ethyl ketone	6
Phenol	6
Benzene	4
Butyl benzyl phthalate	4
bis-(Ethyl hexyl) phthalate	4
Chlorobenzene	4
1,1,1-Trichloroethane	4
Aniline	3
Benzyl chloride	3
Diethylphthalate	2
Phthalic anhydride	2
21 other POHCs including:	1 each
Amines	
Chlordane	
Chlorobenzenes	
Chloromethane	
Chloroethanes	
Cresol(s)	
Dimethyl phenol	
Dodecanol	
Hexachlorobutadiene	
Hexachlorocyclopentadiene	
Isocyanates	
Methylene bromide	
Methyl pyridine	

* Total number of waste streams = 22.

PICs at one or more sites. PIC mechanisms, discussed below, might increase emission rates resulting in a lower calculated DRE. Seventeen of the 20 points on Figure 3 that are below 99.99% DRE were for cases where one or both of these factors were present. The other three points were between 99.97 and 99.99%.

For this program PICs were defined as EPA-listed compounds found in the stack effluent but not found in the waste above 100 ppm. Some PICs were found at every site. Table 5 lists the PICs found and shows the number of sites at which they were found and the concentrations measured for each test run.

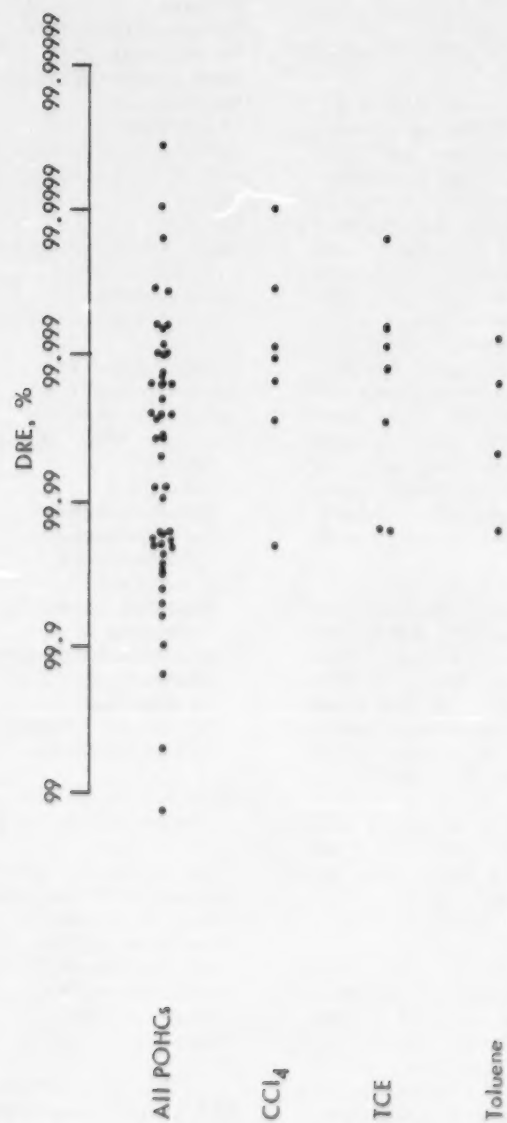


Figure 3. DRE Ranges

TABLE 3. PICs FOUND IN STACK EFFLUENTS

PIC	Number of sites	Concentrations (ng/L)
Benzene	5	< 0.6-112
Chloroform	5	1-1,000
Bromodichloromethane	3	3-32
Dibromochloromethane	3	1-12
Bromoform	2	0.2-10
Methylene chloride	2	2-27
Naphthalene	2	5-100
o-Nitrophenol	2	25-50
Phenol	2	4-22
Bromochloromethane	1	14
Carbon disulfide	1	32
Methylene bromide	1	19
2,4,6-Trichlorophenol	1	110
17 other PICs	1 to 2	< 10

Thirteen different PICs were found at a concentration of at least 10 ng/L at one or more sites. Seventeen other PICs were found at concentrations below 10 ng/L. There are several possible ways to explain the presence of PICs in the stack effluents. One is that they actually are PICs or compounds formed in the complex combustion reactions. A second possibility is that the compounds were present in the waste below detection levels and were destroyed at a relatively low DRE. A compound present in the waste at a concentration just below the detection level of 100 ppm and subject to 99.9% DRE would be present in the stack effluent at a detectable level of about 10 ng/L. Thus, it would be identified as a PIC. A third possibility is that the compounds may have been introduced to the incineration system from some source other than the waste. An example is chlorinated compounds in city water used for scrubbers. Some of the data indicated this possibility was very likely for some compounds at specific sites. One or any combination of these possibilities could affect the emission of PICs in any given case.

Figure 4 compares the relative concentrations of POMCs and PICs measured for each test run. The concentrations of both cover a wide range, but the two ranges are similar. PIC concentrations are grouped more than the POMC concentrations are in the 1- to 10 ng/L range, with 33 of the 48 points in that range.

At selected plants the concentrations of POMCs were measured in scrubber and ash effluents. The data are very limited, but they indicate that most POMCs were not detected in these effluents. When POMCs were detected they tended to be toluene, phenol, or naphthalene at low concentrations. Calculations generally show that the quantities emitted in these effluents are small compared to the quantities emitted from the stack.

OTHER POLLUTANT EMISSIONS

Carbon monoxide and total hydrocarbon levels were also monitored continuously during the tests. Table 6 shows the concentrations measured. The ranges were broad, but the values were relatively low at most sites, below 15 ppm for CO and below 10 ppm for THC. At some sites an additional test run was made at altered combustion conditions; e.g., lower temperature or different combustion airflows. For one of these runs, CO and THC levels as high as 4,000 and 250 ppm, respectively, were observed.

Particulate concentrations varied widely from site to site depending on the presence and efficiency of control devices, the amount of ash suspended in the gas stream, and other factors. Table 7 shows the range of average results for sites with and without control devices. Sites

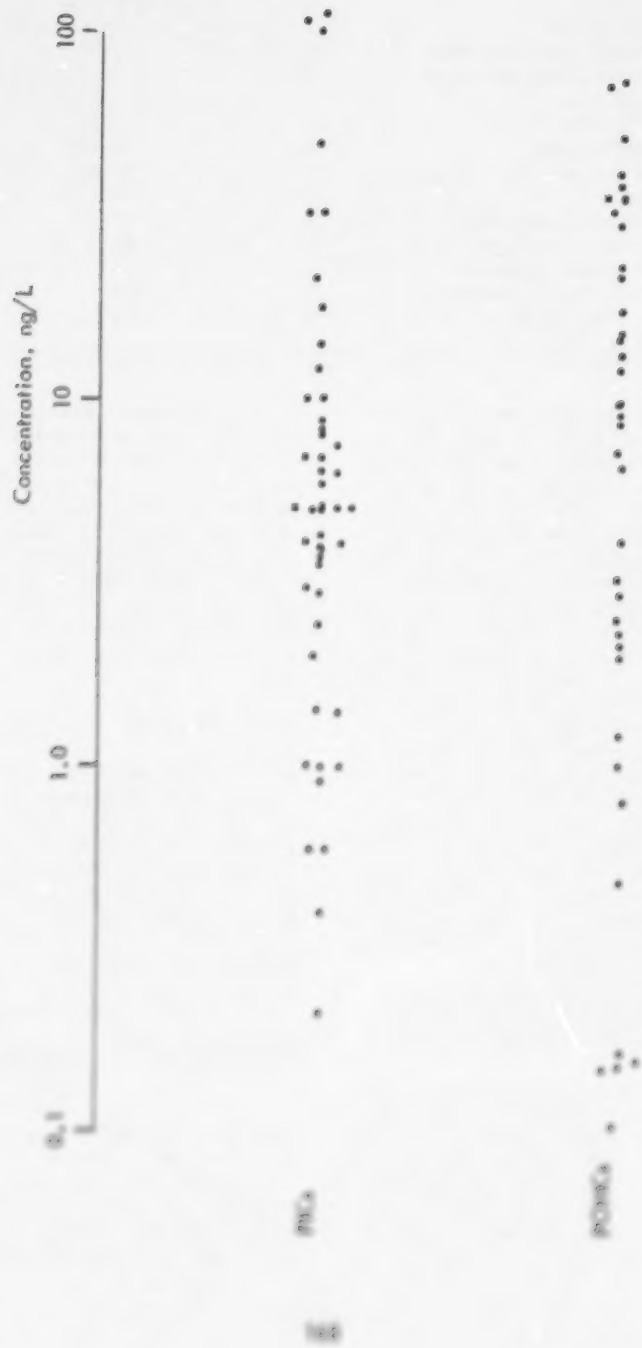


Figure 4. PCB and PIC Concentration in Stack Effluent

TABLE 6. CARBON MONOXIDE AND TOTAL HYDRO-CARBON CONCENTRATIONS IN STACK EFFLUENTS

Pollutant	Range of values (test averages)
CO	1 - 570 ppm: most values below 15 ppm
THC	< 1 - 60 ppm: most values below 10 ppm

TABLE 7. PARTICULATE CONCENTRATIONS IN STACK EFFLUENT*

	Range of values (test averages)
Four incinerators without a control device	60 - 900 mg/dscm (0.03 - 0.39 gr/dscf)
Four incinerators with control devices	20 - 400 mg/dscm (0.01 - 0.17 gr/dscf)

* Corrected to 7% oxygen.

with control devices generally had lower emissions, though the ranges overlapped considerably. This overlap reflects the variety of interacting factors that affect particulate emission levels.

Table 8 shows the average test results for chloride emission and chloride removal efficiency. At all sites the emission rates were near or below 2 kg/h (4 lb/h). All of these sites where significant amounts of chlorinated compounds were burned have scrubbers and typically achieved 99% efficiency or better.

At four of the sites waste and particulate emissions were analyzed for selected metals. Table 9 shows some

metals frequently detected. As the table shows, nickel, chromium, barium, and lead were the metals most often found in the waste streams. Concentrations varied widely from barely detectable up to about 1% for lead in one waste. Stack emissions are also shown on the table and are expressed as a percentage of the input rate for each metal. This value is likely influenced by the degree of suspension and control of particulates and possibly by the selective removal of specific metals due to differences in particle size or solubility of the metal compounds in scrubber liquids.

CONCLUSION

Combustion of hazardous waste in incinerators is a complex process. A very large number of interacting parameters potentially have an effect on the DRE and emission levels. Thus, to detect trends or relationships is difficult, and will require further data analysis. Some conclusions that can be drawn at this time, however, are:

1. A minimum DRE for hazardous waste incinerators under the combinations of operating conditions encountered is at least 99%.

2. DREs below 99.99% often result when the concentration of a POC in the waste is less than 1,000 ppm.

3. DREs below 99.99% occur more often for compounds typically identified as PICs than for other POCs.

4. Chloroform in city water used as makeup for scrubbers can contribute to stack emissions and result in a lower DRE for that compound.

Further data analysis is being conducted which will expand on the conclusions from this data base. EPA expects to have a background document with the results of this analysis available by the end of the year.

TABLE 8. CHLORIDE RESULTS

	Emission rate		Efficiency (%)
	lb/h	kg/h	
Three incinerators without control devices	0.007-4.3	0.003-1.9	-
Five incinerators with control devices	0.3-2.3	0.1-1.1	98-99.9

TABLE 9. METALS FOUND IN WASTES AT FOUR SITES

Metal	Number of waste streams	Waste feed concentration range, µg/g	Stack emissions as a percent of input
Nickel	12	0.01-6.670	0.2-53
Chromium	10	0.1-2.170	0.4-35
Barium	9	< 1-1,460	0.1-6
Lead	7	1-9,830	2-20
Cadmium	4	0.01-224	0.1-2
Antimony	4	< 10-64	< 1-7
Selenium	2	< 100-380	6

FLUIDIZED-BED INCINERATOR PERFORMANCE EVALUATION

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ABSTRACT

A sampling and analysis program was conducted to assess the performance of a fluidized-bed hazardous waste incinerator. Union Chemical, Inc., designed and built the incinerator to destroy the organic portion of the wastes produced by their solvent recycling business. During the test program, 5.2 kg/min (11.5 lb/min) of wastes containing 9.6 percent chlorine were burned. The principal volatile chlorinated organics in the feed were 1,1,2-trichloro-1,2,2-trifluoroethane (3.0 percent), 1,1,1-trichloroethane (3.4 percent), trichloroethylene (2.4 percent), and tetrachloroethylene (3.3 percent). Flue gas samples were collected, for analysis of volatile organics, with the Volatile Organic Sampling Train and Tedlar bags. Particulate and HCl emissions were sampled with a modified Method 5 train. Results are presented in this paper.

INTRODUCTION

Fluidized-bed incinerators have been used in the petroleum and paper industries, for the processing of nuclear wastes and by municipalities for sewage sludge disposal. Solids, liquids, and gases can be burned in fluidized beds. However, the technology is most applicable to waste that are difficult to burn in a simple liquid injection incinerator or to waste streams that do not require a rotary kiln system. Sludges or slurries with high concentrations of suspended solids, high water content, low heating value, or high viscosity are good candidates for fluidized-bed incineration. Short-term fluctuations in the above properties can be tolerated by a fluidized bed without major adverse effects on operating efficiency.

A field sampling program was conducted on June 30 and July 1, 1982, to assess the performance of a fluidized-bed hazardous waste incinerator. The tests were conducted on an 82 m (32 in.) diameter incinerator under normal operating conditions. The primary objectives of the test program were to:

1. Determine whether or not the incinerator was achieving at least 99.99 percent destruction/removal efficiency for selected difficult-to-incinerate, volatile, chlorinated organic compounds;
2. Measure HCl removal efficiency; and
3. Measure particulate emissions.

Three replicate tests were planned.

SITE DESCRIPTION

Union Chemical Company, Inc., is a commercial solvent reprocessing/waste disposal business located in Union, Maine. Waste solvents are received in tank trucks or drums from generators in the New England area. The electronics industries located in Massachusetts and southern New Hampshire are the major sources of spent solvents. The Seave site includes an analytical laboratory; tank truck loading and unloading facilities; drum han-

dling and storage areas; thin film evaporators for reprocessing spent solvents; tanks for handling fuel, spent solvents, clean solvents, and water; and the fluidized-bed incinerator. The thin film evaporators are used to reprocess nonchlorinated and chlorinated solvents.

Residues from the evaporators and solvents not suitable for reprocessing are burned either in a boiler (which helps heat the evaporators) or in the fluidized-bed incinerator. Any chlorinated wastes are burned in the incinerator, after blending to limit the chlorine content to less than about 12 percent. Potential water runoff from the site is collected and fed to the incinerator to destroy trace organic compounds.

Figure 1 is a simplified schematic of the incinerator and the associated emission control systems. An oil-fired burner is used to start up the incinerator. When the freeboard temperature reaches

650°C (1200°F), flammable nonchlorinated solvents are fed to the bed and the oil burner is turned off. Incineration of chlorinated wastes is started when the freeboard temperature reaches 1090°C (2000°F). Typical temperatures measured, by existing plant instruments, during the test program, are shown in Figure 1. Temperature modulation is achieved by controlling the ratio of combustion air to waste feed, the dirty water feed rate, and the distribution of combustion air between the primary supply and each of the overfire air injection heights.

The fluidized-bed combustor is a refractory lined cylindrical vessel with a height of 7.3 m (24 ft) and an inside diameter that varies from 0.81 m (32 in.) to 1.1 m (42 in.). The bed material consists of about 0.6 m (2 ft) of less than 16 mesh silica sand. Combustible wastes are fed to the bed through a single nozzle. Dirty water is added separately. The temperature profile in the combustor and experience with other fluidized-bed combustors indicate that volatil-

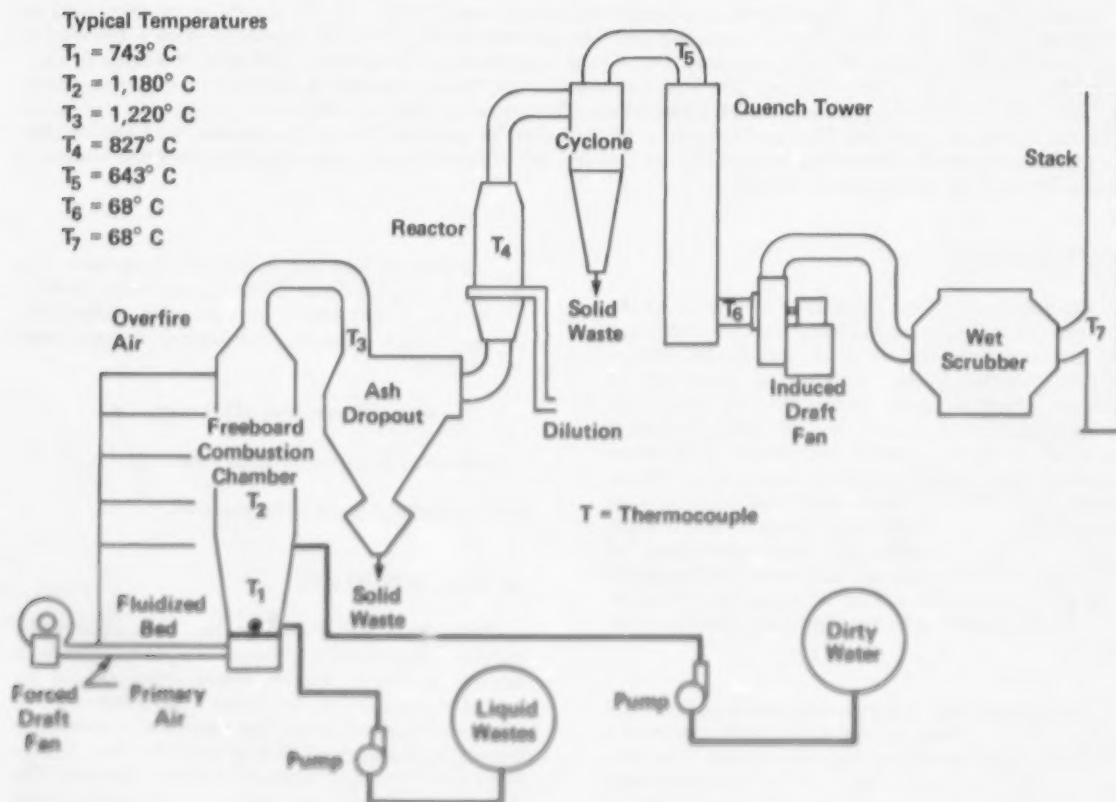


Figure 1. Schematic of Union Chemical fluidized bed incineration system.

ization occurs in the bed while combustion begins in the bed and is completed in the freeboard.

During the test program, waste feed and dirty water feed rates averaged 5.2 kg/min (11.5 lb/min) and 4.7 kg/min (10.4 lb/min), respectively. Heat input from the waste feed was 2.2 MW (7.6×10^6 Btu/hr). Oxygen concentration, after the addition of overfire air, was estimated to be 9.5 percent based on the measured stack concentration, stack flow, and dilution airflow. Under these conditions, the average gas residence time is estimated at $1\frac{1}{2}$ seconds above 1100°C (2000°F). This residence time includes the combustor and ash dropout.

Dilution air is added to the reactor vessel to begin cooling the flue gases. Lime was formerly added with the dilution air for HCl removal but did not prove to be effective. Most of the particulates are collected in the Fisher Klosterman XQ high-efficiency cyclone. The combustor ash dropout, reactor, cyclone, and the top of the quench tower are refractory lined.

Lime slurry is sprayed into the top of the quench tower to control HCl emissions. In addition, there are several spray nozzles that are turned on and off as needed to control temperature.

The final control device is a Celicote FRP cross-flow wet scrubber containing 1.2 m (4 ft) of Tellerette packing. During the test program, some NaOH was added to the cross-flow scrubber for final HCl removal.

FEED STREAMS

Drums of solvent wastes were premixed and their contents stored in a continuously stirred 5700-liter (1500-gallon) tank. The same waste feed was used for each of the three $1\frac{1}{2}$ - to 2-hour test runs. During each run, samples of the waste feed and dirty water feed were collected, in volatile organic analysis (VOA) vials, at 30-minute intervals. Results were based on the analysis of one waste feed composite and three dirty water samples for each run. The waste feed rate was determined from the rate of change of the level in the storage tank, and the dirty water feed rate was determined from a flow meter.

The waste feed samples were analyzed for volatile organics by a method similar to A101b (Sampling and Analysis Methods for Hazardous Waste Incineration) [Harris et al. (1)]. The waste feed was dispersed in purified tetraglyme (tetraethylene glycol dimethyl ether), followed by dilution in water and standard purge and trap GC/MS procedures. Dirty water samples were analyzed for volatile organics by standard purge and trap GC/MS procedures (EPA Method 824, 41 CFR 186).

Analysis for chlorine, in all streams, was done by ion chromatography. Waste feed composites were prepared for chlorine analysis by Parr oxygen bomb combustion as outlined in ASTM D808-63. The dirty water samples did not require preparation for chlorine analysis.

Results for the waste feed and dirty water feed analyses are presented in Table 1. The average waste feed contained 3.0 percent 1,1,2-trichloro-1,2,2-trifluoroethane, 3.4 percent 1,1,1-trichloroethane, 2.4 percent trichloroethylene, and 3.3 percent tetrachloroethylene. The quantity of these compounds in the dirty water was not significant when compared to the waste feed, as shown in Table 1. The chlorine content of the waste feed averaged 9.64 percent and the dirty water contained 0.466 percent chlorine.

FLUE GAS EMISSIONS

Particulate and HCl

A modified Method 5 train was used to determine particulate and HCl emissions. The modified Method 5 train included impingers that contained NaOH to trap HCl. The flue gas sampling location was more than 8 duct diameters downstream and 2 duct diameters upstream from the nearest flow disturbance. Therefore, only 12 traverse points were needed as flow disturbances were not significant. Integrated gas samples were collected in Tedlar bags for O_2 and CO_2 analyses in accordance with EPA Method 3. Ion chromatography was used to measure chlorine in the impingers.

The average particulate concentration was 1100 mg/dscm (0.49 gr/dscf) corrected to 7 percent O_2 . Recent discussions with Union Chemical representatives indicate that they have been able to reduce particulate emissions to 180 mg/dscm (0.08 gr/dscf) by modifying the quench tower exit and the cross-flow scrubber.

The average HCl removal efficiency of the incinerator system was 99.73 percent, as shown in Table 2. Mass emissions averaged 0.087 kg/hr (0.19 lb/hr) of HCl. These removal efficiencies and emission rates meet, with a margin of safety, the regulatory requirements of 99 percent efficiency or 1.9 kg/hr (4 lb/hr).

Volatile Organic Compounds

Sampling and analysis for very low concentrations of volatile organic compounds in a flue gas matrix at a hazardous waste site required the application of some nonstandard or developmental methods. An integrated gas sample train using Tedlar bags and the Volatile Organic Sampling Train (VOST) were used.

TABLE 1. FEED RATES AND COMPOSITIONS—MAJOR CHLORINATED VOLATILE ORGANICS

	Run 1		Run 2		Run 3		Average (g/min)
	See footnotes	g/min	See footnotes	g/min	See footnotes	g/min	
Waste Feed							
Total	13.1 ^a	5,940	10.3 ^a	4,670	11.0 ^a	4,990	5,200
1,1,2-Trichloro- 1,2,2-trifluoroethane	2.8 ^b	166	2.6 ^b	122	3.7 ^b	185	158
1,1,1-Trichloroethane	3.3 ^b	196	3.4 ^b	159	3.4 ^b	170	175
Trichloroethylene	2.2 ^b	131	2.4 ^b	112	2.6 ^b	130	124
Tetrachloroethylene	3.0 ^b	178	3.0 ^b	140	4.0 ^b	200	173
Chlorine	9.7 ^b	576	9.5 ^b	445	9.7 ^b	484	52
Dirty Water Feed							
Total	14.7 ^c	6,660	8.34 ^c	3,790	8.26 ^c	3,750	4,730
1,1,2-Trichloro- 1,2,2-trifluoroethane	0.0004 ^d	0.03	0.0003 ^e	0.01	0.0004 ^e	0.01	0.02
1,1,1-Trichloroethane	0.0032 ^d	0.21	0.0037 ^e	0.14	0.0034 ^e	0.13	0.16
Trichloroethylene	0.0005 ^d	0.03	0.0005 ^e	0.02	0.0006 ^e	0.02	0.02
Tetrachloroethylene	0.0002 ^d	0.01	0.0002 ^e	0.008	0.0002 ^e	0.007	0.008
Chlorine	0.452 ^b	30.1	0.466 ^b	17.6	0.480 ^b	18.0	21.9
Total Feed							
1,1,2-Trichloro- 1,2,2-trifluoroethane	—	166	—	122	—	185	58
1,1,1-Trichloroethane	—	196	—	159	—	170	75
Trichloroethylene	—	131	—	112	—	130	24
Tetrachloroethylene	—	178	—	140	—	200	73
Chlorine	—	606	—	463	—	502	24

^a Pounds per hour based on volumetric flow and a measured specific gravity of 1.12 g/cm³.^b Analysis of composite sample reported as percent.^c Pounds per hour based on volumetric flow and specific gravity of 1.0 g/cm³.^d Analysis of two samples, reported as percent by weight.^e Analysis of three samples, reported as percent by weight.

TABLE 2. CHLORINE RESULTS

	Run 1	Run 2	Run 3	Average
Waste Feed				
Total, g/min	5,940	4,670	4,990	200
Chlorine, percent	9.70	9.53	9.59	—
g/min	576	445	484	502
Dirty Water Feed				
Total, g/min	6,660	3,790	3,750	730
Chlorine, percent	0.632	0.666	0.680	—
g/min	20	15	15	22
Flue Gas				
Total, m ³ /min	74.0	105	94.5	92.0
Chlorine, g/m ³	11,000	10,000	12,000	—
g/min	0.80	0.05	1.26	1.41
Removal Efficiency, percent	99.85	99.91	99.75	99.72

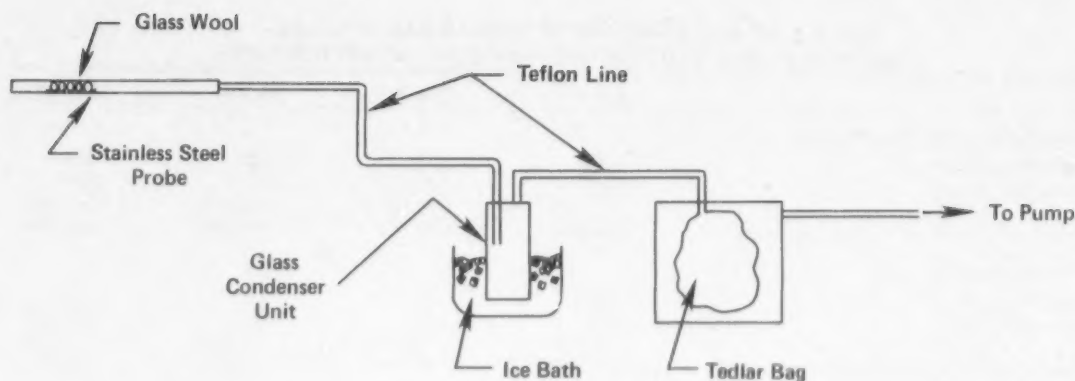


Figure 2. Integrated gas sampling train.

Two parallel integrated gas sampling trains were used as shown in Figure 2. The 20-liter bags were filled at a constant rate over the test runs. Because sample degradation was considered to be a potential problem, the Tedlar bag samples were returned to GCA's laboratory and analyzed within 48 hours for run 1, 8 hours for run 2, and 24 hours for run 3. Condensate collected before the bags was reserved for analysis by standard purge and trap GC/MS techniques. Initial gas analyses were conducted by gas chromatography with electron capture detection (GC/ECD). Each of the gas samples was then pumped over Tenax cartridges and reserved for thermal desorption GC/MS analysis. Because very low concentrations of organics were anticipated, only one Tenax cartridge was used for each bag. The objectives of Tenax cartridge GC/MS analyses were to confirm the identity of the four principal volatile organics, provide qualitative and quantitative measurements of other volatile constituents, and provide data on both groups of compounds should the GC/ECD fail to meet the detection limit objectives because of interference from other organic compounds or water vapor.

The GC/ECD analysis was conducted with a 1-percent SP-1000 Carbowax column and an argon/methane (95/5) carrier gas. A temperature programmed analysis was chosen for the GC/ECD analysis in order to provide separation for the lower boiling point components while maintaining a reasonable run time for the higher boiling components. At the lower end of the calibration curve, temperature programming was not compatible with the electron capture detector. As a consequence, the instrumental detection limits were higher than expected. The results of the integrated gas sampling train analyses show that 1,1,2-trichloro-1,2,2-trifluoroethane was less than $300 \mu\text{g}/\text{m}^3$, trichloroethylene was less than $1200 \mu\text{g}/\text{m}^3$, and tetrachloroethylene was less than

$750 \mu\text{g}/\text{m}^3$. The above values are strictly a function of the GC/ECD operation; actual emissions could be far below the instrumental detection limits noted above. During run 1, 1,1,1-trichloroethane was below the detection limit of $200 \mu\text{g}/\text{m}^3$ while during runs 2 and 3, 260 to $540 \mu\text{g}/\text{m}^3$ were detected. Note that blank values for the bag samples were not obtained and that subsequent tests at other sites have shown that contamination is possible.

The destruction/removal efficiency, based on the GC/ECD analysis, for 1,1,2-trichloro-1,2,2-trifluoroethane was greater than 99.980 percent, trichloroethylene was greater than 99.903 percent, and tetrachloroethylene was greater than 99.960 percent, as shown in Table 3. Average destruction/removal efficiency for 1,1,1-trichloroethane appeared to be 99.983 percent. The GC/ECD detection limits did not allow us to determine whether or not the incinerator was achieving 99.99 percent destruction/removal efficiency. In current field sampling programs at other sites, we are using a column that does not require temperature programming and are achieving detection limits that are one to two orders of magnitude better, depending on the compound.

Tenax cartridges that were used to adsorb organics in the Tedlar bag samples were thermally desorbed into the GC/MS system. However, data were not obtained for the four major constituents because an early eluting compound exceeded the mass spectrometer capacity, causing the system to shut down. This problem is discussed in more detail later.

The second flue gas sampling and analysis method consisted of one of the first field trials of the Volatile Organic Sampling Train (VOST). This method involves the collection of organics from the flue gas on Tenax and Tenax-charcoal cartridges, as

**TABLE 3. GC/ECD ANALYSES OF TEDLAR BAG SAMPLES –
CHEMICAL FLOWS AND DESTRUCTION/REMOVAL EFFICIENCIES**

	Run 1	Run 2	Run 3	Average
1,1,2-Trichloro-1,2,2-trifluoroethane				
Feed rate, g/min ^a	166	122	185	158
Emissions, $\mu\text{g}/\text{m}^3$	< 350 ^c	< 350 ^c	< 350 ^c	< 350 ^c
g/min ^b	< 0.027	< 0.037	< 0.033	< 0.032
Destruction/Removal efficiency, percent	> 99.984	> 99.970	> 99.982	> 99.980
1,1,1-Trichloroethane				
Feed rate, g/min ^a	196	159	170	175
Emissions, $\mu\text{g}/\text{m}^3$	< 200 ^c	325	480	270-335
g/min ^b	< 0.015	0.034	0.045	0.029
Destruction/Removal efficiency, percent	> 99.992	99.979	99.974	99.983
Trichloroethylene				
Feed rate, g/min ^a	131	112	130	124
Emissions, $\mu\text{g}/\text{m}^3$	< 1,300 ^c	< 1,300 ^c	< 1,300 ^c	< 1,300 ^c
g/min ^b	< 0.10	< 0.14	< 0.12	< 0.12
Destruction/Removal efficiency, percent	> 99.924	> 99.88	> 99.907	> 99.903
Tetrachloroethylene				
Feed rate, g/min ^a	178	140	200	173
Emissions, $\mu\text{g}/\text{m}^3$	< 750 ^c	< 750 ^c	< 750 ^c	< 750 ^c
g/min ^b	< 0.057	< 0.079	< 0.071	< 0.069
Destruction/Removal efficiency, percent	> 99.967	> 99.944	> 99.965	> 99.960

^a Based on Table 1.

^b Based on the indicated concentrations and gas flows of 76.6 m³/min for run 1, 105 m³/min for run 2, and 94.5 m³/min for run 3.

^c Worst case estimate of emission concentration based on detection limit of the GC/ECD system that was used for analysis.

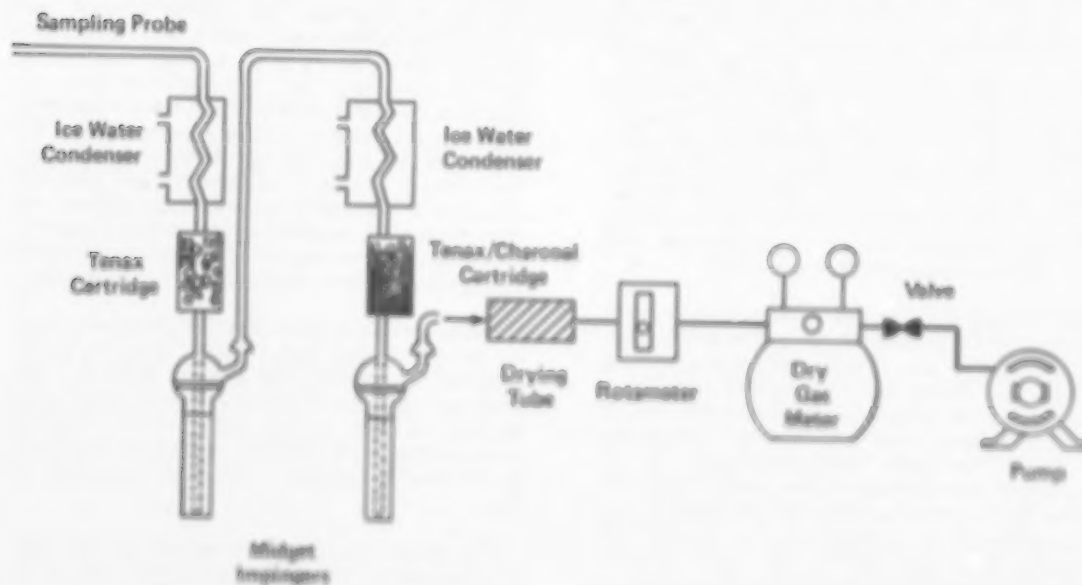


Figure 2. Schematic of volatile organic sampling train.

shown in Figure 3. Each set of cartridges was replaced with fresh cartridges at 20-minute intervals. Analysis was conducted by thermal desorption GC/MS.

Two types of blank cartridges were analyzed. Laboratory or method blanks consisted of Tenax and Tenax/charcoal cartridges that were sealed in screw-cap culture tubes and transported with the sample cartridges. The laboratory or method blanks were not opened at the site. Field-biased blanks were also sealed in culture tubes during transport but were opened for about 30 seconds, and handled onsite in a manner similar to the handling of the sample cartridges. During this program, and other early EPA-sponsored tests of this sampling train, problems were encountered with field contamination of blank samples. The field-biased blanks that were handled onsite in a manner similar to the test cartridges showed high blank values for all test compounds. In some cases, the blank values exceeded the sample values. The method blanks that were never opened outside the laboratory showed high concentrations of 1,1,1-trichloroethane. Analytical results are shown in Table 4.

Although the VOST samples cannot be used to quantify emissions, they can be used to develop some useful worst case calculations of emissions and to place lower bounds on the destruction/removal

efficiency. For this purpose, it is assumed that the chemicals on the sample cartridges represent actual emissions. A blank correction is not applied. This is a worst case calculation because it assumes that there is no sample contamination although the blank sample cartridges do show high levels of contamination.

The results of the above calculation are shown in Table 5 for three of the test compounds. Results are not reported for 1,1,1-trichloroethane because some of the blanks and samples exceeded the maximum calibration range of the GC/MS. The VOST train results indicate that destruction removal efficiency for 1,1,2-trichloro-1,2,2-trifluoroethane was greater than 99.993 percent, trichloroethylene was greater than 99.985 percent, and tetrachloroethylene was greater than 99.994 percent.

Methylene chloride measurements were also conducted but have been affected by especially severe contamination. The VOST blanks and samples all contained quantities of methylene chloride above the calibration range of the GC/MS. The Tedlar bag samples and the condensate collected prior to the bags also contained relatively large quantities of methylene chloride. Data on heat of combustion indicate that the destruction efficiency of methylene chloride should be similar to the other four test compounds and, therefore, emission concentrations

TABLE 4. RESULTS OF VOST TRAIN ANALYSES

Run Number	1,1,2-Trichloro-1,2,2-trifluoroethane (ng/tube) ^a	Trichloroethylene (ng/tube) ^a	Tetrachloroethylene (ng/tube) ^a
Method Blank	<200	<200	<200
Field Biased Blank	3,700	>9,000	7,000
1A ^b	2,450	5,900	2,000
1B ^b	1,700	4,000	1,900
1C ^b	2,000	1,000	000
Total Run 1	6,150	11,700	3,200
2A ^b	1,000	5,000	2,700
2B ^b	2,100	6,000	2,970
2C ^b	2,100	2,000	000
Total Run 2	5,000	13,000	5,300
3A ^b	1,000	5,070	2,000
3B ^b	2,000	6,000	5,300
3C ^b	2,000	000	000
Total Run 3	5,000	6,000	5,000

^aDuring each run, a total of 60 liters of gas was sampled. Therefore, the total ng per run can be converted to $\mu\text{g}/\text{m}^3$ by dividing by 60.

^bBecause the blank values were so high, these data represent uncorrected results or worst case emission measurements.

**TABLE 5. GC/MS ANALYSES OF VOST SAMPLES—
CHEMICAL FLOWS AND DESTRUCTION/REMOVAL EFFICIENCIES**

	Run 1	Run 2	Run 3	Average
1,1,2-Trichloro-1,2,2-trifluoroethane				
Feed rate, g/min ^a	166	122	185	158
Emissions, µg/m ³	<100 ^c	<100 ^c	<140 ^c	<120 ^c
g/min ^b	<0.0079	<0.0106	<0.013	<0.010
Destruction/Removal efficiency, percent	>99.9952	>99.9913	>99.9928	>99.9931
Trichloroethylene				
Feed rate, g/min ^a	131	112	130	124
Emissions, µg/m ³	<195 ^c	<234 ^c	<157 ^c	<200 ^c
g/min ^b	<0.015	<0.025	<0.015	<0.018
Destruction/Removal efficiency, percent	>99.989	>99.978	>99.989	>99.985
Trichloroethylene				
Feed rate, g/min ^a	178	140	200	173
Emissions, µg/m ³	<87 ^c	<110 ^c	<92 ^c	<96 ^c
g/min ^b	<0.0066	<0.011	<0.0087	<0.0088
Destruction/Removal efficiency, percent	>99.9963	>99.9918	>99.9957	>99.9946

^aBased on Table 1.

^bBased on the indicated concentrations and gas flows of 76.6 m³/min for run 1, 105 m³/min for run 2, and 94.5 m³/min for run 3.

^cWorst case estimate, of emission concentrations based on VOST train results that have not been corrected for high blank values.

should have been less than 1 percent of the values that appear to have been measured. If the methylene chloride was being emitted from the incinerator, then significant concentrations should have been found in the scrubber water, but none was detected. In addition, methylene chloride has often caused problems in analysis of water samples because clean samples may become contaminated from methylene chloride in industrial and/or laboratory environments. There is sufficient doubt about the validity of the methylene chloride results such that useful conclusions cannot be developed at this time.

SUMMARY OF RESULTS AND CONCLUSIONS

A summary of the destruction/removal efficiency results for both the integrated gas samples (Tedlar bags and GC/ECD analysis) and the VOST is presented in Table 6. Conclusions are presented below:

- The measurement of low concentrations of volatile chlorinated organic compounds in the incinerator flue gas presented some unexpected

TABLE 6. SUMMARY OF DESTRUCTION/REMOVAL EFFICIENCY RESULTS^a

Compound	Destruction/Removal efficiency (percent)	Emission concentrations	
		µg/m ³	ppb
Tedlar Bag Sample			
1,1,2 Trichloro-1,2 trifluoroethane	> 99.990	< 360 ^b	< 40
1,1,1 Trichloroethane	99.983	310	52
Trichloroethylene	> 99.993	< 1,300 ^b	< 210
Perchloroethylene	> 99.990	< 750 ^b	< 100
Volatile Organic Sampling Train			
1,1,2 Trichloro-1,2 trifluoroethane	> 99.990 ^d	< 130 ^d	< 14 ^d
1,1,1 Trichloroethane			
Trichloroethylene	> 99.980	< 360 ^d	< 52
Perchloroethylene	> 99.9946	< 96 ^d	< 13

^aConcns are not reported for methylene chloride because severe sample contamination is suspected.

^bWorst case estimated emission concentration based on detection limit of the GC/ECD system that was used for analysis.

^cWorst case estimate of emission concentrations based on VOST train results that have not been corrected for high blank values.

^dResults are not available due to severe sample contamination.

problems. Detection limits of the GC/ECD system were too high to quantitate flue gas concentrations or to demonstrate 99.99 percent destruction. Therefore, GC/ECD detection limits were used to place upper bounds on the emission concentrations and lower bounds on the destruction efficiency. VOST blanks showed high concentrations of volatile organic compounds relative to the samples. The VOST sample results were used, without blank correction, to place upper bounds on the emission concentrations and to place lower bounds on the destruction efficiency.

- Analysis of integrated gas samples by GC/ECD shows that destruction/removal efficiency for 1,1,2-trichloro-1,2,2-trifluoroethane exceeded 99.98 percent. VOST results indicate that destruction/removal efficiency exceeded 99.99 percent.
- Analysis of integrated gas samples by GC/ECD shows that destruction/removal efficiency for 1,1,1-trichloroethane was about 99.98 percent. This result does not include correction for bag blank concentrations.
- Analysis of integrated gas samples by GC/ECD shows that destruction/removal efficiency for trichloroethylene exceeded 99.90 percent. VOST results indicate that destruction/removal efficiency exceeded 99.985 percent.
- Analysis of integrated gas samples by GC/ECD shows that destruction/removal efficiency for tetrachloroethylene exceeded 99.96 percent. VOST results indicate that destruction/removal efficiency exceeded 99.99 percent.

- Methylene chloride measurements were inconclusive. Extreme sample contamination is suspected.
- HCl removal efficiency averaged 99.72 percent, and emissions averaged 0.19 lb/hr.
- Particulate emissions averaged 1100 mg/dscm (0.49 gr/dscf) corrected to 7 percent O₂.

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FULL-SCALE BOILER EMISSIONS TESTING OF HAZARDOUS WASTE COFIRING

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ABSTRACT

Cofiring of certain hazardous wastes with heat recovery in industrial boilers may be a promising way to comply with Resource Conservation and Recovery Act (RCRA) provisions for safe waste disposal while recovering useful energy. To explore the feasibility and possible environmental side effects of cofiring, the Incineration Research Branch of the U.S. EPA is sponsoring full-scale field sampling and analysis tests of boiler waste cofiring.

Several boiler design types and waste compositions are being tested to identify compatible waste/boiler combinations for cofiring. The sampling protocol includes continuous monitor measurements of stack concentrations of O_2 , CO, CO_2 , NO_x , and total hydrocarbons; modified EPA Method 5 measurements of particulates, and grab samples of fuel, waste and ash streams. Principal organic hazardous constituents (POHC's) are absorbed onto two organic sorbent traps built into sampling trains. During post-test chemical analyses, gas chromatography/mass spectrometry (GC/MS) is used on all inlet and outlet samples to allow computation of the destruction and removal efficiency (DRE) of selected POHC's in the waste. Three boilers have been tested: a 10,000 lb/hr wood-waste-fired watertube unit cofired with creosote waste residue; an 8,400 lb/hr gas-fired firetube unit cofired with alkyd resin wastewater; and a 230,000 lb/hr gas-fired watertube unit cofired with phenolic residue wastes. Analytical results for the three tests are discussed in this paper. Most of the hazardous compounds present in large concentrations in the waste were destroyed and/or removed to an efficiency in the vicinity of 99.99 percent. Destruction and removal efficiencies were generally lower for the wood-fired unit than for the two gas-fired units.

CONCLUSIONS

The initial three tests discussed here were designed to explore the operational feasibility and waste destruction efficiency for routine "as found" boiler operation typical of current industrial cofiring practice. As such, the boilers exhibited excursions in excess combustion air, waste flowrate and load. No significant operational problems attributable to cofiring were observed during the 1-week duration of each boiler test. Boiler thermal efficiency was generally unaffected by cofiring except in the one case where the waste had a water

content greater than 90 percent. This water resulted in increased latent heat losses out the stack which reduced boiler efficiency by 10 percent.

The destruction and removal efficiencies varied from 99 to 99.999 percent depending on the boiler tested and the composition and concentration of the principal organic hazardous constituents. In several cases, it appeared that compounds present in higher concentrations exhibited higher DRE than compounds present in trace quantities.

The mass weighted DRE for RCRA Appendix VIII compounds varied from 99.98 percent for a wood-fired boiler to 99.998 percent for a gas-fired watertube. The combustion conditions, particularly high excess air, low load and transient operation, were not necessarily conducive to efficient waste destruction. Higher DRE may be achievable if a boiler is specifically tuned for waste cofiring.

The test results indicate the potential for achieving a DRE of 99.99 percent for certain boiler/waste combinations. The range of conditions tested so far, however, is narrow. The organic waste heat of combustion for all tests was approximately 9.2 kCal/g, although one waste was mixed with water yielding a heat of combustion for the water-organic waste blend of 9.02 kCal/g. Any further testing should broaden the data base to other boiler/fuel/waste combinations. Particular data needs are: chlorinated wastes with low heats of combustion; oil- and coal-fired boilers; and evaluation of the effects of transient operating conditions on DRE.

INTRODUCTION

Thermal destruction of wastes by direct incineration or by cofiring in boilers, furnaces, or kilns can be an economical alternative to landfills or chemical treatment. Direct incineration of hazardous wastes is regulated by Part 264 of the RCRA which was adopted in January 1981 although boiler cofiring is currently exempted from RCRA provisions. The incineration rules limit atmospheric emissions in order to minimize the environmental effects of solid or liquid waste disposal. Specifically, principle organic hazardous constituents (POHC's) in the waste must exhibit a destruction and removal efficiency (DRE) of ≥ 99.99 percent, defined as:

$$DRE = (W_{\text{feed}} - W_{\text{stack}}) / W_{\text{feed}} \times 100$$

where

W_{feed} = mass rate of flow of a POHC in the waste

W_{stack} = stack mass emission rate of a POHC

POHC's are those compounds listed in appendix VIII of the May 1980 RCRA amendments which are present in significant

concentrations in the waste. This specification of DRE gives credit for POHC removal in ash streams although the ash may then require evaluation. For chlorinated wastes, the RCRA rules also require control of chloride emissions.

Since many hazardous wastes have significant heating value, they have a potential value if cofired with conventional fuels in boilers for heat recovery. This, in principle, can be an attractive alternative to incineration while meeting the RCRA goal of resource recovery. The benefits of cofiring include partial replacement of conventional fuels and the use of existing boilers in industries where incinerators are not available. Although boiler cofiring is currently not regulated, the need for inclusion in RCRA provisions is currently being studied by EPA. To support this study, the tests discussed in this paper are being conducted as part of the thermal destruction R&D program managed by EPA's Incineration Research Branch in Cincinnati.

The overall objective of the test program discussed here is to evaluate the operational feasibility and destruction efficiency of boiler cofiring for hazardous waste disposal. The desired output is a tabulation of boiler design types, fuels, and operating conditions which will achieve a satisfactory DRE for a given hazardous waste. Toward this goal, field measurements of DRE are being made on selected boiler-waste combinations. To limit the field measurement effort to a manageable size, a parallel pilot-scale parametric test program is being conducted to screen combustion characteristics and waste characteristics which influence thermal destruction. This pilot-scale screening is essential because the existing population of boiler designs and operating conditions is very diverse. E.g., the candidate boiler design-fuel-waste combinations of potential interest number in the thousands. Accordingly, the pilot-scale tests will be used to guide field test site selection and to help evaluate the pilot-scale results. Conducting the pilot and field efforts in parallel rather than in series is desirable because the pilot-scale tests cannot completely simulate all parameters thought to influence thermal destruction. Thus, the field tests provide a verification or judgment aid on the translation of

pilot-scale results to full-scale DRE. The pilot-scale effort is documented in a separate paper presented at this symposium(1).

FIELD TEST PROGRAM

Site Selection

Initial test sites were selected to obtain a preliminary evaluation of waste destruction feasibility over a broad range of boiler designs and waste characteristics. As pilot-scale results become available, subsequent site selection will be focused on specific boiler-waste combinations needed to efficiently establish the limits of destruction efficiency. For the preliminary site selection, boiler operators firing hazardous wastes were identified and facility specifications were obtained. These candidates were screened based on the following criteria:

- Availability and accessibility of the boiler for testing
- Proportion of hazardous constituents in the waste according to RCRA Appendix VIII specifications
- Estimated degree of difficulty in destroying POHC's efficiently
- Degree to which the boiler-fuel type is representative of future widespread use for waste cofiring

An earlier EPA study(2) was used for guidance in evaluating the third and fourth criteria. Candidates ranking high in at least three of the criteria were evaluated further by a pretest site survey. Where exact waste compositions were not available, waste samples were obtained and analyzed. From this procedure, three sites were selected:

- Site 1 -- 4,500 kg/hr (10,000 lb/hr) Keeler watertube fired with wood bark and cofired with creosote waste
- Site 2 -- 3,800 kg/hr (8,400 lb/hr) Cleaver Brooks firetube fired with natural gas and cofired with alkyd resin paint waste

- Site 3 -- 105,000 kg/hr (230,000 lb/hr) Babcock and Wilcox watertube fired with natural gas and cofired with phenol wastes

Design and operating characteristics are summarized in Table 1. Tests at these sites were conducted during the period of March to July 1982. Chemical analyses of the samples from these tests are available and discussed here. Additional boiler tests are in progress.

Sampling and Analysis Protocol

Four test runs were made at each site: a baseline test with conventional fuel only and no waste, and triplicate cofiring runs with the boiler operated at approximately the same conditions. The baseline test was run to establish the difference in emissions due to cofiring. For all runs, the boiler was operated as in routine practice. No attempt was made to constrain the boiler to a fixed load or excess air level beyond routine practice. This was done so that the DRE's measured would be representative of real-world operation rather than exemplary conditions.

The sampling protocol was designed to obtain POHC concentrations at all influent and effluent streams. Grab samples of the waste feed, and (for the wood-fired boiler) the fuel, bottom ash, and particulate collector hopper ash were taken throughout each of the 5-hour test runs and composited for analysis. Continuous monitor measurements of O₂, NO, CO, CO₂, and unburned hydrocarbons were made for the flue gas. Sampling was done upstream of the preheater, if present. The continuous monitors as specified in Table 2 were housed in a mobile sampling laboratory. These measurements are useful to augment control room board data as a continuous record of boiler operation. NO_x and CO, in particular, are quite sensitive to combustion conditions, and NO_x (decreasing) or CO (increasing) may correlate with conditions which promote POHC breakthrough.

Organic constituents were sampled using two separate trains extracting flue gases from ports in the stack. Low molecular weight volatile organics were sampled using a Tenax train depicted in Figure 1. Flue gases were drawn at 200 cc/min through the Tenax tube

TABLE 1. BOILER DESIGN AND OPERATING CHARACTERISTICS

Site	1	2	3
<u>Design characteristics:</u>			
• Manufacturer/boiler type	Keeler CP-308 watertube-stoker balanced draft	Cleaver Brooks 250-hp firetube	Babcock and Wilcox watertube balanced draft
• Heat input capacity, MW_t (10^6 Btu/hr)	3.5 (12)	2.9 (10)	82 (280)
• Rated steam capacity, 10^3 kg/hr (10^3 lb/hr)	4.5 (10)	3.8 (8.4)	105 (230)
• Air pollution control device	Multiclone	None	None
<u>Operating characteristics:</u>			
• Primary fuel	Woodwaste (hog)	Natural gas	Natural gas
• Waste fuel	Creosote sludge	Alkyd resin wastewater	Phenolic residue
• Waste fuel heat of combustion, ΔH Kcal/g (Btu/lb)	9.28 (16,700)	0.02* (35)	9.2 (16,600)
• Waste fuel moisture content, percent	24 [†]	>99*	<1
• Operating steam load, percent of capacity	100	25	25
• Waste fuel heat input, percent of total	40	<1*	37-39
• Excess combustion air, percent	100	30	85
• Volumetric heat release rate, MW_t/m^3 (10^3 Btu/hr-ft ³)	300 (29)	750 (72)	78 (7.5)
• Estimated furnace bulk residence time, $\bar{\tau}$ sec	1.2 ^{††}	0.8 ^{††}	>2 ^{††}
• Outlet streams sampled	Flue gas, bottom ash, flyash	Flue gas	Flue gas

*Typical, although highly variable as result of nonhomogeneity of organics in wastewater.

[†]Portion of moisture content is attributed to highly volatile organics.

^{††}Gross estimate to indicate relative magnitude of bulk residence time in each boiler. $\bar{\tau}$ calculated by $V/\dot{Q}$ at a furnace temperature of 1,650K (2,500°F).

TABLE 2. CONTINUOUS MONITORING EQUIPMENT

Instrument	Principle of operation	Manufacturer	Instrument model	Range
NO NO _x	Chemiluminescence	Thermo Electron	10 AR	0-100 ppm 0-500 ppm 0-1,000 ppm 0-5,000 ppm
CO	Nondispersive infrared (NDIR)	ANARAD	500R	0-1,000 ppm
CO ₂	Nondispersive infrared (NDIR)	ANARAD	AR500	0-20 percent
TUHC	Flame ionization	Beckman	400	0-1,000 ppm
O ₂	Fuel cell	Teledyne		0-5 percent 0-25 percent

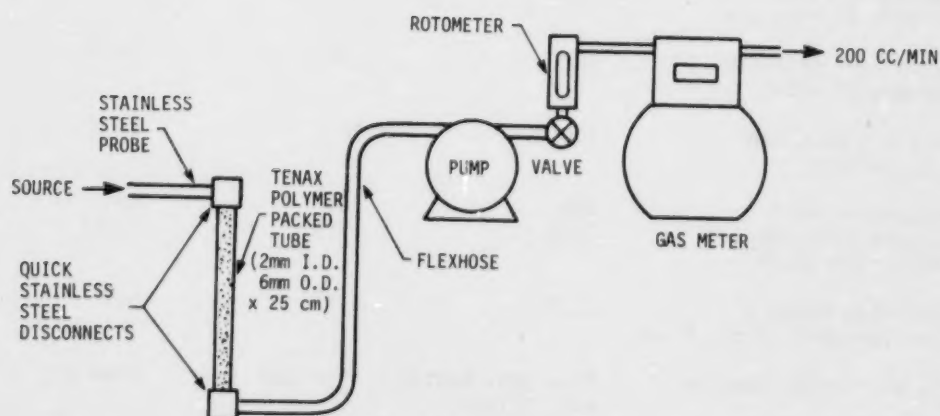


Figure 1. Porous polymer vapor sampling method.

containing approximately 2g of sorbent until the total sample gas volume exceeded 2 liters. Higher molecular weight organics (>C₇ with boiling range >110°C) were sampled using an XAD-2 organic sorbent module positioned at the back of the EPA Method 5 train as shown in Figure 2. A quantity of about 65g XAD-2 was packed in the glass module through which flue gas was extracted isokinetically at approximately 200 ml/s. A total sample volume of >5 dry standard cubic meters (dscm) was extracted.

In the analytical laboratory, the Tenax traps were thermally desorbed at the head of a packed column gas chromatograph (GC) by heating to 180°C. Volatile compounds desorbed from the Tenax traps were subsequently separated by heating the GC column and were detected in a mass spectrometer (MS) operating in a continuous scanning mode. With this technique detection limits were normally 50 ng per sample. Modified Method 5 samples (probe catch, filter, XAD, and impinger solutions) were extracted separately for base/neutral and acid semivolatile and nonvolatile compounds using methylene chloride in a soxhlet apparatus. Extracts were combined and concentrated. Organic analyses were performed by GC/MS using a fused silica capillary column (FSCC). Waste fuel organics were extracted using liquid/liquid extractors also with methylene chloride, concentrated, and analyzed by capillary GC/MS. Detection limits for semi and nonvolatile organics were generally 1 to 5 ng per sample. Analyses of duplicate, blind spiked, and blank samples were performed as part of the quality assurance/quality control (QA/QC) protocol.

FIELD TEST RESULTS

Site 1 Results

The wood-fired boiler at site 1 was operated at full load with the creosote waste contributing approximately 40 percent of the total heat input to the boiler and wood contributing approximately 60 percent. Table 3 summarizes semivolatile and nonvolatile organic flowrates measured in the flue gas and combined ash streams during the baseline test. The compounds listed are those which showed a significant concentration in either the flue gas for the baseline test, or in the creosote

waste. Organics which are part of the RCRA Appendix VIII hazardous compound list are grouped separately from other semivolatile and nonvolatile organics. Hazardous organics detected in the flue gas during combustion of wood only were found to be phenol, 2,4-dimethylphenol, naphthalene and nitrobenzene. For the most part, these compounds were also found in each ash stream. Additionally, pentachlorophenol was also detected in the flyash. This is attributed to wood partially contaminated with creosote. Due to the relative magnitude of the stream, organic flowrates in the flue gas were much higher than in either or combined ash streams.

Table 4 summarizes organic compound flowrates and flue gas-based DRE's calculated for one of the three cofired test runs. Results from the other two test runs are similar to the ones shown here. DRE's were calculated based on flue gas emission rates over and above those attributable to wood only. That is, the difference in flue gas emissions between the cofiring test and the baseline test was used in calculating the actual DRE of compounds in the feed. The weighted average DRE for Appendix VIII compounds was less than 99.99 percent. Only phenol was found to exceed 99.999 percent destruction. DRE's of most other organics also ranged between 99.9 and 99.99. A trend toward lower DRE with lower waste concentration may be deduced from these results.

Volatile organic analyses showed the presence of toluene in all three cofired tests with emission flowrates varying from 27 to 480 µg/s (8 to 140 µg/dscm). Other volatile compounds appearing in only one or two tests were benzene at 450 µg/s, ethylbenzene at 330 µg/s, and chlorobenzene at 14 µg/s.

Dioxin Testing

Additional site 1 analyses were done to screen for the presence of chlorinated dibenzodioxins since these compounds are often associated with creosote and pentachlorophenol. The overall screen was positive, so Battelle Columbus Laboratories was contracted to quantitate specific isomers and to speciate 2,3,7,8 TCDD. Results for one of the runs are summarized in Table 5. In the waste, dioxins tended to predominate in the higher isomers -- hepta-CDD and octa-CDD. In the flue gas, the reverse was evident; dioxin concentration

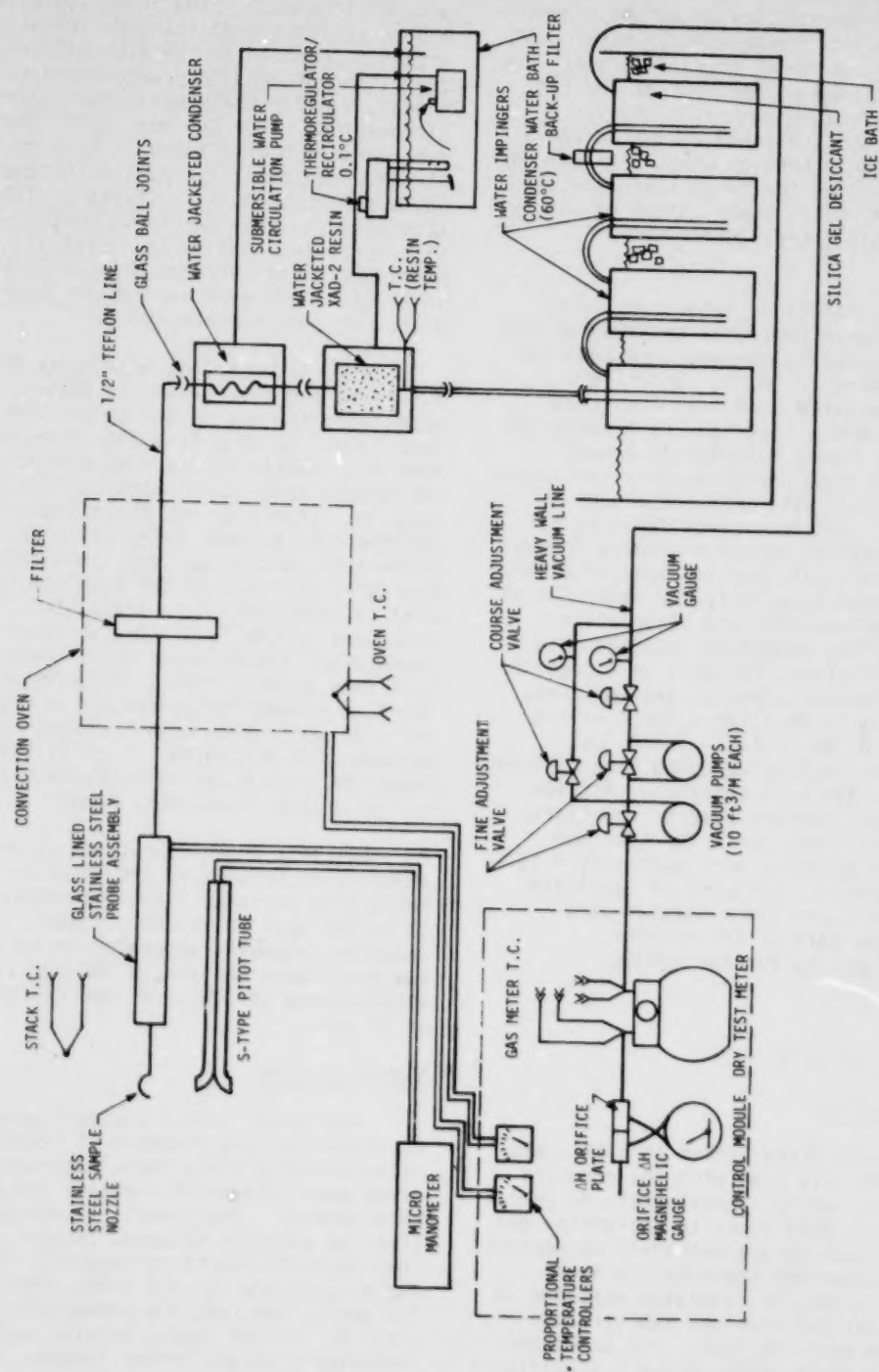


Figure 2. Modified EPA Method 5 train.

TABLE 3. SITE 1 -- BASELINE TEST EMISSIONS (WOOD WASTE ONLY)

Compound	Flue gas		Bottom ash ($\mu\text{g/kg}$)	Flyash ($\mu\text{g/kg}$)
	ppb	$\mu\text{g/s}$		
RCRA Appendix VIII				
Naphthalene	1.5	25	320	1,200
Pentachlorophenol	ND	<3.2	ND	1,200
Phenol	18	220	80	100
2,4-Dimethylphenol	0.83	13	ND	40
4-Nitrophenol	ND	<13	ND	40
Fluoranthene	ND	<0.6	ND	ND
Nitrobenzene	0.28	4.5	60	ND
Other semivolatiles and nonvolatiles				
Biphenyl	ND	<6.4	ND	ND
Pyrene	ND	<0.6	ND	ND
Phenanthrene	ND	<0.6	ND	1,300
Fluorene	ND	<0.6	ND	20
Anthracene	ND	<0.6	ND	20
Methylpyrene	ND	<6.4	ND	180
Dibenzofuran	ND	0.6	ND	200
Cyclopenta(d,e,f)phenanthrene	ND	<6.4	ND	ND
Acenaphthene	ND	<0.6	ND	20
Acenaphthylene	ND	<3.2	ND	20
Diphenylamine	ND	<6.4	ND	40
2-Nitrophenol	0.90	16	ND	ND
4-Chloro-m-cresol	0.60	11	ND	ND
Methylnaphthalene	0.07	1.3	20	40
Methylphenol	1.7	24	ND	ND
Hydroxymethoxybenzaldehyde	3.0	58	380	ND
Benzoic acid	3.1	49	ND	ND

ND = Not detected. For flue gas, the concentration was below 0.03 ppb for most compounds except for pentachlorophenol, 4-nitrophenol, biphenyl, methylpyrene, cyclopenta(d,e,f)phenanthrene and acenaphthylene for which ND is less than 0.3 ppb. For ash streams ND is generally less than 2.0 $\mu\text{g/kg}$.

TABLE 4. SITE 1 -- DRE'S FOR COFIRING WOOD WASTE AND CREOSOTE

Compound	Creosote waste ($\mu\text{g/ml}$)*	Flue gas		DRE (percent)
		ppb	$\mu\text{g/s}$	
<u>RCRA Appendix VIII</u>				
Naphthalene	6,000	2.0	35	99.997
Pentachlorophenol	2,200	0.77	28	99.975
Phenol	800	0.20	2.5	>99.999
2,4-Dimethylphenol	360	<0.19	<3.2	>99.98
4-Nitrophenol	200	0.79	15	99.85
Fluoranthene	60	0.83	23	99.2
Weighted average DRE	. . .	. . .	. . .	>99.98
<u>Other major semivolatiles and nonvolatiles[†]</u>				
Biphenyl	8,400	<0.30	<6.3	>99.999
Pyrene	8,400	0.54	15	99.996
Phenanthrene	7,000	2.9	70	99.980
Fluorene	5,000	1.5	34	99.986
Anthracene	3,000	0.58	14	99.991
Methylpyrenes	1,600	0.04	1.3	99.998
Weighted average DRE	. . .	. . .	. . .	99.992
<u>Other minor semivolatiles and nonvolatiles^{††}</u>				
Dibenzofuran	880	1.5	34	99.92
Cyclopenta(d,e,f)phenanthrene	620	0.08	2.5	99.992
Acenaphthene	160	1.2	26	99.67
Acenaphthylene	140	<0.03	<0.6	>99.991
Diphenylamine	120	0.06	1.3	99.98
Weighted average DRE	. . .	. . .	. . .	99.93

*To obtain feedrate in $\mu\text{g/s}$ multiply $\mu\text{g/ml}$ concentration by 50 ml/s.

[†]Major compounds whose measured concentration was greater than 1,000 ppm (1,000 $\mu\text{g/ml}$) in the creosote waste.

^{††}Minor compounds with <1,000 ppm concentration.

tended toward the lower isomers -- tetra-CDD and penta-CDD. This suggests the possibility that during the combustion process the higher isomers in the waste are reduced to lower isomers. This would account for the low DRE (negative in the case of tetra-CDD) for the lower isomers. The overall DRE for dioxins was comparable to the DRE for the waste as a whole.

Continuous monitor results for site 1 showed large variations in operating conditions over the test run. Flue gas O_2 levels varied from 6.2 to 16.7 percent with a corresponding rise in CO from 230 to >1,000 ppm. These abnormally high levels of excess air will probably produce some quenching in the flame which would also promote breakthrough of organics. The DRE values exhibited in these tests may be improved if the boilers were tuned for higher efficiency.

Site 2 Results

The site 2 firetube boiler was operated at a load of 2,000 lb steam/hr, which is approximately a quarter load. This off-load operation would produce opposing effects on DRE of reduced temperature and longer residence time. Table 6 summarizes emissions measured during the baseline test run with only natural gas combustion. Detected semivolatile and nonvolatile organics were found to have flowrates less than 4 $\mu\text{g/s}$ corresponding to flue gas concentrations between 1 and 4 ppb. Toluene and naphthalene were the only two POHC's detected. Table 7 summarizes the organics flowrates and DRE's for one of the three cofired test runs using alkyd resin waste water. Heat input attributable to the waste was less than 1 percent based on waste composition generally consisting of about 99 percent water. Here, weighted average DRE's of the POHC's and other organics in the wastewater generally exceeded 99.99 percent. The other two cofired test runs show similar semivolatile and nonvolatile organic emission results. Volatile organics detected during this test were methylene chloride and hexane. Methylene chloride is a suspected contami-

nant because it was not detected in the other cofiring tests. Hexane is a product of incomplete natural gas combustion through flame quenching.

Site 3 Results

The 230,000 lb/hr watertube boiler at site 3 was operated off-load at 60,000 lb/hr with four of the six burners in service. During cofiring the phenolic residue was injected through one of the four burners. The other three operated on gas only. Combustion air was fed through all six burners. Phenolic residue contributed approximately 40 percent of the total heat load to the boiler. To improve the heat absorption profile in the boiler at low load, the excess air was increased to a level corresponding to 10 percent O_2 . Baseline test results in Table 8 show that phenolic, phthalate and benzene compounds were the major organic emissions with flue gas concentrations generally less than 2 ppb. DRE during cofiring, summarized in Table 9, generally exceeded 99.99 percent, even at this off-spec operation. For many of the compounds, including phenol the major POHC, the DRE exceeded 99.999.

ACKNOWLEDGMENTS

This work was sponsored by the U.S. Environmental Protection Agency under contracts 68-03-3043 and 68-03-3176. George L. Huffman and Robert A. Olexsey were the Project Officers, and assisted in all phases of the project.

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TABLE 5. SITE 1 DIOXIN RESULTS

Isomer	Emissions (ug/s)			DRE (percent)
	Waste	Flue gas	Bottom ash	
2,3,7,8 TCDD	ND	ND	NA	ND
Tetra-CDD	ND	0.14	ND	...
Penta-CDD	0.10	0.044	ND	56.0
Hexa-CDD	18	0.024	ND	99.87
Hepta-CDD	180	0.017	0.0048	99.99
Octa-CDD	170	0.014	0.014	99.99
Total CDD	370	0.24	0.020	99.94

NA -- Not analyzed.

ND -- Compound concentration was below the detectable limit in the waste (0.0032 ug/s) or in the bottom ash (0.000088 ug/s).

TABLE 6. SITE 2 -- BASELINE TEST (NATURAL GAS ONLY)

Compound	Flue gas outlet	
	ppb	ug/s
<u>RCRA Appendix VIII</u>		
Toluene	1.7	2.3
Naphthalene	1.3	2.4
Pentachlorophenol	ND	<0.23
<u>Other semivolatiles and nonvolatiles</u>		
Xylenes	2.4	3.7
C ₃ -Alkylbenzenes	0.20	0.32
C ₄ -Alkylbenzenes	0.09	0.18
Benzoic acid	ND	<0.45
Benzaldehyde	0.60	0.90
Ethylbenzaldehyde	3.7	2.4
1,2-Benzenedicarboxylic acid	ND	<0.45
Methyl-1,1-biphenyl	ND	<0.05
Methylnaphthalenes	0.18	0.36

ND = Not detected. Detection limit corresponds to 0.06 ppb for pentachlorophenol, 0.26 ppb for benzoic acid, 0.20 ppb for 1,2-benzenedicarboxylic acid and 0.02 ppb for methyl-1,1-biphenyl.

TABLE 7. Site 2 -- DRE'S FOR COFIRING NATURAL GAS AND ALKYD RESIN

Compound	Alkyd resin wastewater ($\mu\text{g/ml}$)*	Flue gas		DRE† (percent)
		ppb	$\mu\text{g/s}$	
<u>RCRA Appendix VIII</u>				
Toluene	0.3-550 (186)	1.2	1.6	>99.999
Naphthalene	0.07-1.7 (0.62)	1.2	2.1	>99.8
Pentachlorophenol	0.02-0.29 (0.18)	<0.05	<0.2	>97
Weighted average DRE	. . .	. . .	. . .	>99.995
<u>Other semivolatiles and nonvolatiles</u>				
Xylenes	268-2,760 (1,770)	3.4	5.1	99.997
Benzoic acid	310-1,190 (870)	<2.7	<4.6	>99.98
C ₃ -Alkylbenzene	2-405 (145)	0.77	1.3	99.98
C ₄ -Alkylbenzene	0.10-46 (16)	<0.02	<0.04	>99.99
Methyl-1,1-biphenyl	0.-0.7 (0.25)	<0.02	<0.02	>99.5
1,2-Benzenedicarboxylic acid	0.-0.32 (0.20)	<0.15	<0.35	>94
Methylnaphthalenes	0.-0.17 (0.06)	0.26	0.53	91
Benzaldehyde	0.-0.08 (0.03)	0.80	1.2	70
Weighted average DRE	. . .	. . .	. . .	>99.990

*Range in concentration is based on analysis results of three separate waste residue samples collected during the test. Concentration in parenthesis represents arithmetic average. To obtain feedrate in $\mu\text{g/s}$ multiply by 33.5 ml/s.

†DRE is based on average concentration of compound in the alkyd resin wastewater.

TABLE 8. SITE 3 -- BASELINE TEST (NATURAL GAS ONLY)

Compound	Emissions	
	ppb	µg/s
<u>RCRA Appendix VIII</u>		
Phenol	0.63	32
Dibutylphthalate	0.32	49
Bis(2-ethylhexyl)phthalate	1.7	370
<u>Other semivolatiles and nonvolatiles</u>		
C ₃ -Alkylbenzene*	2.1	140
C ₃ -Alkylbenzene*	ND	<8
Benzene acetaldehyde	ND	<8
2,2'-Methylenebisphenol	0.01	1.6
4,4'-Methylenebisphenol	0.04	5
Pyrene	ND	<2
C ₁₅ H ₁₆ O*	ND	<8
C ₁₅ H ₁₆ O*	ND	<8
C ₁₈ H ₂₀	ND	<8
C ₁₆ H ₁₈ O	ND	<8

*Different isomers.

ND = Not detected. Detection limit corresponds to about 0.10 ppb or 8 µg/s.

TABLE 9. SITE 3 -- DRE'S FOR COFIRING NATURAL GAS AND PHENOLIC RESIDUE

Compound	Phenolic residue ($\mu\text{g/ml}$)*	Flue gas		DRE (percent)
		ppb	$\mu\text{g/s}$	
<u>RCRA Appendix VIII</u>				
Phenol	53,000	0.30	28	>99.999
Dibutylphthalate	120	1.4	220	99.4
Bis(2-ethylhexyl)phthalate	31	1.2	260	>99.98
Weighted average DRE	. . .	. . .	. . .	>99.998
<u>Other major semivolatiles and nonvolatiles[†]</u>				
C ₃ -Alkylbenzene ^{††}	100,000	0.93	61	>99.999
C ₃ -Alkylbenzene ^{††}	45,000	<0.10	<8	>99.999
Benzene acetaldehyde	5,000	<0.12	<8	>99.999
C ₁₆ H ₁₈ O	>38,000	<0.07	<8	>99.999
C ₁₈ H ₂₀	>34,000	<0.06	<8	>99.999
C ₁₅ H ₁₆ O ^{††}	7,500	<0.07	<8	>99.999
C ₁₅ H ₁₆ O ^{††}	3,000	<0.07	<8	>99.999
Weighted average DRE	. . .	. . .	. . .	>99.999
<u>Other minor semivolatiles and nonvolatiles[#]</u>				
2,2'-Methylenebisphenol	460	<0.07	<8	>99.993
4,4'-Methylenebisphenol	370	<0.07	<8	>99.991
Pyrene	4	0.05	5	99.5
Weighted average DRE	. . .	. . .	. . .	>99.990

*To obtain feedrate in $\mu\text{g/s}$ multiply concentration in $\mu\text{g/ml}$ by 250 ml/s.

[†]Major compounds whose measured concentration was greater than 1,000 ppm.

^{††}Different isomers.

[#]Minor compounds with <1,000 ppm concentration.

SUBSCALE PARAMETRIC STUDIES ON THE COMBUSTION OF HAZARDOUS WASTES

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ABSTRACT

Thermal destruction of wastes by cofiring with conventional fuels in boilers, furnaces, or kilns have several attractions. The ability of such devices to destroy wastes to environmentally acceptable levels is not well documented. This study looks at the effects of operational variables of a subscale furnace on time-temperature regimes in order to estimate the impact of the variables on destruction efficiencies in full-scale units. Over 50 different combinations of firing rate, excess air rate, waste-to-fuel ratio, waterwall surface area, burner swirl setting, and waste type have been investigated.

Preliminary information suggests that excess air rate and firing rate will play the most significant parts in establishing destruction efficiencies.

INTRODUCTION

Thermal destruction of wastes by direct incineration or by cofiring with conventional fuels in boilers, furnaces, or kilns is one of the most effective methods currently available for disposal of hazardous organic material. While direct incineration of hazardous wastes is regulated by Part 264 of the Resource Conservation and Recovery Act (RCRA) as adopted in January 1981, boiler cofiring is currently exempt from RCRA provisions. However, the potential for boiler cofiring regulations is being evaluated by the Environmental Protection Agency (EPA). To support these efforts, EPA's Incineration Research Branch (IRB) in conjunction with the Office of Solid Waste is conducting a research and development programs on incineration effectiveness and regulatory impact analyses of which the tests discussed in this paper are a part.

The overall objective of this test study is to evaluate the effectiveness of boiler cofiring as a means of hazardous waste destruction and removal. This evaluation will correlate such parameters as boiler design types, fuels, and operating conditions which will achieve a desired destruction and removal efficiency (DRE) for a given principal organic hazardous component (POHC) in the waste. POHC's are those compounds listed in Appendix VIII of the May 1980 RCRA amendments, and DRE is defined as:

$$DRE = (M_{\text{feed}} - M_{\text{stack}}) / M_{\text{feed}} \times 100$$

where

M_{feed} = Mass flowrate of a POHC
in the fuel

M_{stack} = Stack mass emission rate
of a POHC

Although it is intuitively known that certain boiler parameters will have a major influence on waste destruction, there is no available collected body of

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data to estimate the magnitude of these influences, either separately or collectively. Time, temperature, and turbulence are the fundamental physical characteristics affecting destruction efficiency. These in turn are determined by such operating parameters as burner configuration and swirl, excess air rate, firing rate, fuel-to-waste ratio, waste effects on flame temperatures, cooling surface-to-combustion volume ratio, etc.

The purpose of the pilot-scale parametric study is to estimate marginal destruction efficiencies as a function of selected operational parameters and to attempt to find methods of correlating the results of pilot tests to full-scale units. This in turn will ultimately assist industry and regulators in permitting the cofiring of wastes in boilers and minimizing the need for full-scale field tests.

This paper briefly describes the pilot-scale parametric test program being conducted, the results obtained to date, and the facility and experimental equipment employed. It should be noted that this is part of a larger integrated study being conducted by Acurex to first

screen the combustion and waste characteristics which influence thermal destruction, then compare with direct in-field measurements of DRE on select boiler-waste combinations, and lastly prepare a semiempirical computer model of thermal destruction.

PROGRAM DESCRIPTION

The current pilot-scale parametric test program is divided into four tasks:

- Baseline time-temperature tests
- Single-compound parametric tests
- Multiple compound parametric tests
- Mathematical simulation

The variables under study in each of the test series are summarized in Table 1. When completed, a total of 74 independent conditions will have been tested, with 58 replicated. All destruction efficiency samples are to be taken in either duplicate or triplicate,

TABLE 1. SUMMARY OF TEST PROGRAM VARIABLES

Task	Independent variables	Dependent variables
Baseline tests	• Flame basket shape • Load • Excess air • Waterwall surface-to-volume ratio	• Temperature profile • Residence times • Exit gas concentrations • Velocity profile
Single-compound tests	• Waste/fuel ratio • Flame basket shape • Load • Excess air • Waterwall surface-to-volume ratio	• Temperature profile • Residence times • Exit gas concentrations • Destruction efficiencies
Multiple compound tests	• Six compounds • Four extreme conditions selected from single-compound tests	• Same as for single-compound tests

and test compound materials are mixed with the base fuel (No. 2 distillate oil) before firing.

The purpose of the baseline tests is to define the thermal environments of the test facility under various operating conditions, to quantify the effects of machine operational variables on the thermal environment, and to gather data to assist in the development of a mathematical simulation. The 10 baseline firing conditions are summarized in Table 2 which include two firing rates (0.23 and 0.37 MW), two excess air rates (10 and 25 percent), three swirl settings (maximum, median, and minimum) and two waterwall surface-to-volume ratios (0 and 0.12).

Compound Tests

The facility DRE was studied using chlorobenzene under the same firing conditions as the baseline tests. Chlorobenzene was fired at two waste-to-fuel ratios (10 and 5 percent v/v). In the multiple compound tests,

five additional compounds will be fired at each of four conditions (10 percent v/v at conditions I, IV, VII, and X). The compounds are tentatively:

- Acrolein
- Pentachlorophenol
- 1,2-Dichloroethane
- Ethyl acrylate
- Acrylonitrile

(Note: At the time of preparation the feasibility of firing mixtures was being studied)

A mathematical simulation of the furnace zone is being assembled. The simulation will predict a time-temperature profile for the bulk gases, and estimate destruction efficiency. It is expected that a boundary layer destruction efficiency calculation will be included.

TABLE 2. BASELINE FIRING CONDITIONS

Condition	Firing rate MW (million Btu/hr)	Excess Air rate (%)	Swirl setting	Waterwall ratio
I	0.37 (1.25)	10	7.5	0
II	0.37 (1.25)	25	7.5	0
III	0.23 (0.8)	10	7.5	0
IV	0.23 (0.8)	25	7.5	0
V	0.23 (0.8)	25	5.0	0
VI	0.23 (0.8)	25	2.5	0
VII	0.37 (1.25)	10	7.5	0.25
VIII	0.37 (1.25)	25	7.5	0.25
IX	0.23 (0.8)	10	7.5	0.25
X	0.23 (0.8)	25	7.5	0.25

RESULTS AND DISCUSSION

Time, temperature, and turbulence (mixing) are the key to understanding the phenomena of thermal destruction. The detailed calculation of destruction performance becomes impractical when attempts are made to apply them to "real world" situations such as the destruction of wastes in boilers. Therefore semiempirical procedures are necessary if one wishes to estimate how changes in operational variables such as firing rate, excess air rate, flame turbulence, and waste-to-fuel ratio affect both the thermal history of the waste and the destruction efficiency of the unit.

The facility used in this study is shown schematically in Figure 1 and described in detail in the following section. It is basically a subscale furnace that approximates linearly a 44-MW packaged "D"-type watertube boiler. Since it is important in estimating destruction efficiency outside the flame to characterize the thermal environment, the tests to date have concentrated on the specific parameter effects on temperature profiles. These are discussed in the following subsections.

Temperature Profiles

For each firing condition, temperature profiles were taken at five cross sections (locations A through E shown in Figure 1). A typical set of profiles as shown in Figure 2 for condition IV indicates a boundary layer temperature zone within 4 inches of the furnace wall. Axial profiles are shown in Figure 3. The importance of this boundary layer cannot be over emphasized at this time, since it represents greater than 43 percent of the volume or thermal environment of the furnace. Because temperature and velocity plays such a large role in volume flowrate and destruction, this zone will be significant when considering destruction efficiencies for this furnace. Preliminary calculations indicate that approximately 20 percent of the volume flow may be in this region.

Gross Effects of Firing Conditions on Temperature Profiles

The centerline axial temperature profiles for the four basic firing conditions are shown in Figure 4. Over the range of conditions tested, the

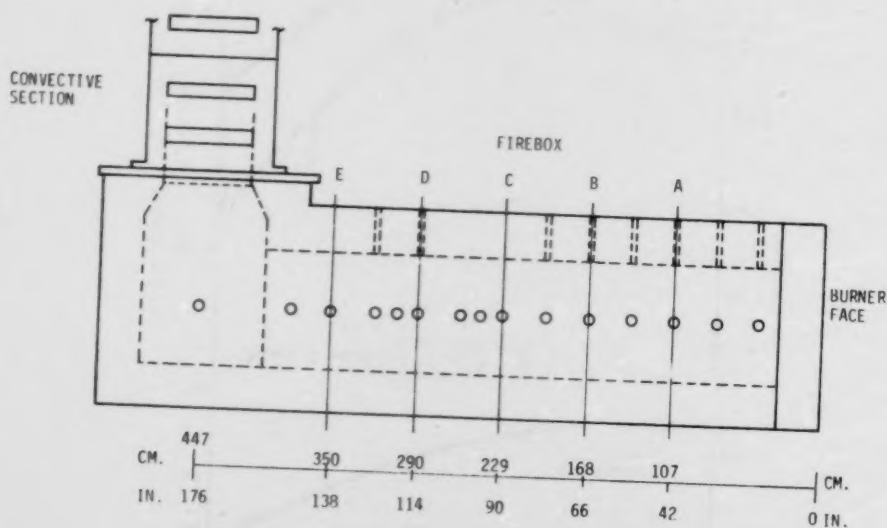


Figure 1. Simplified schematic of subscale furnace showing locations of temperature measurements.

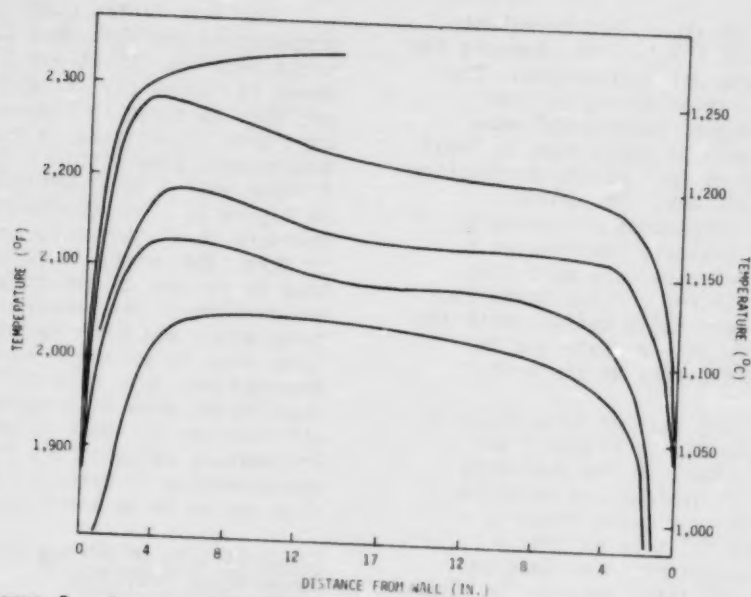


Figure 2. Cross-section temperature profiles for condition IV.

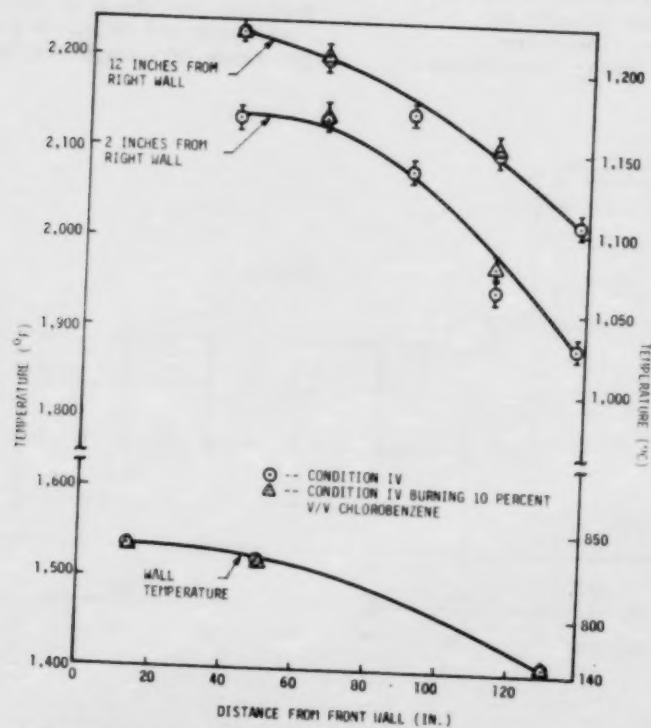


Figure 3. Axial temperature profiles for walls, in boundary layer, and along center line (range of measured values shown by "error" bands).

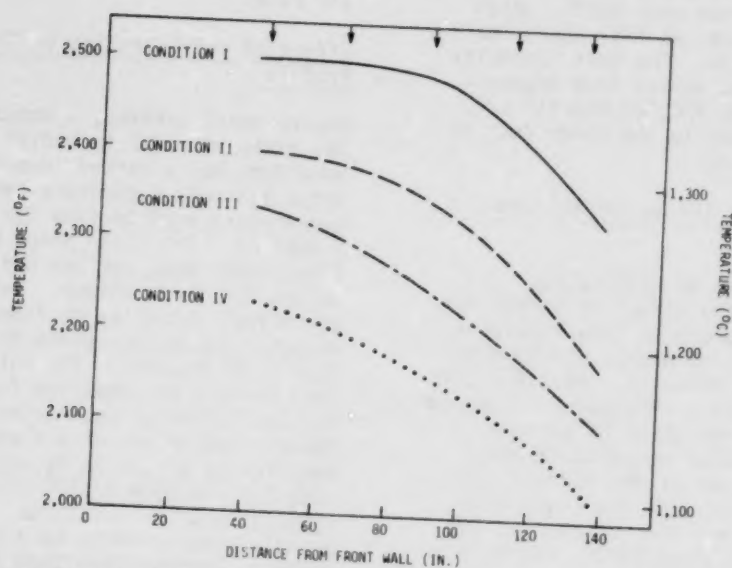


Figure 4. Typical centerline axial temperature profiles for four baseline conditions.

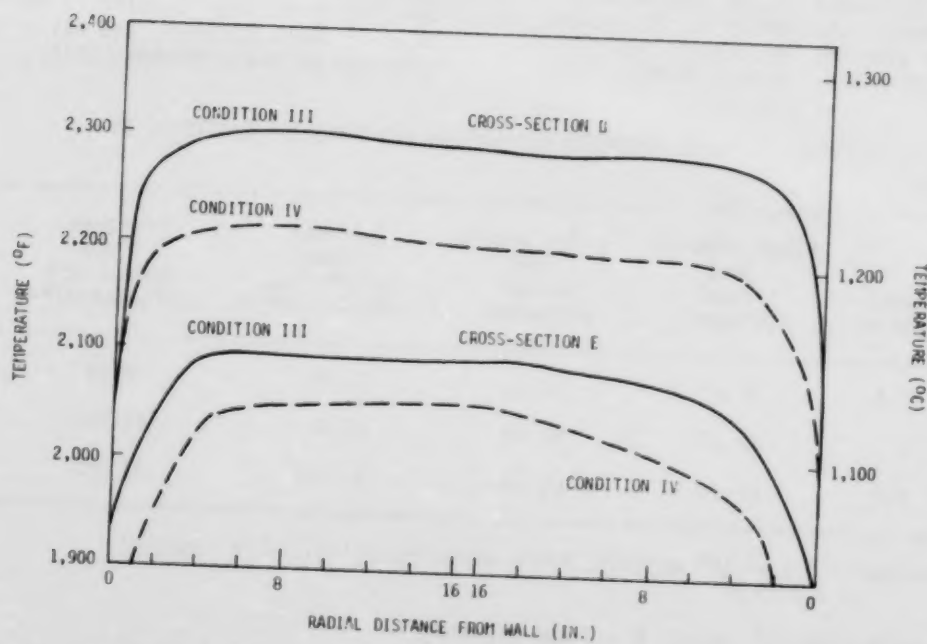


Figure 5. Effects of excess air on temperature profiles (0.8×10^6 Btu/hr and maximum swirl).

furnace front end temperatures varied over approximately 270°F while the exit temperatures varied over 300°F. Mean residence times varied from approximately 3.4 to 5.5 seconds. The heat intensity in the flame zone varied from approximately 140,000 to 220,000 Btu/ft³ hr. This is equivalent to the range seen in industrial boilers.

Effect of Excess Air on Temperature Profiles

There were no qualitative surprises from the effect of excess air on temperature profiles (see Figures 4 and 5). Increasing excess air lowered the temperature profiles. At the higher firing rate (1.25×10^6 Btu/hr) a change of excess air from 10 to 25 percent decreased the axial temperature about 100°F at the front of the furnace and 160°F at the rear. At the lower rate (0.8×10^6 Btu/hr) the decrease at the front was again about 100°F, but at the rear only about 50°F.

Qualitatively these results will have opposing effects on destruction efficiencies. At the higher excess air rate the increased oxygen content will promote destruction while the decreased residence time and temperature will dampen destruction rates. Modeling has

not yet been conducted to determine if there is a peak efficiency with excess air rate.

Effect of Swirl Setting on Thermal Profile

Burner swirl setting, a measure of the ratio of axial to radial air momentum, has a marked impact on flame shape but only a moderate impact on temperature profile (see Table 3 and Figure 6). The flame shape was estimated from visual observations and empirical values for flame volume. Table 3 shows the visual estimates of flame length and diameter under conditions IV (0.8×10^6 Btu/hr). The calculated flame length using the observed flame diameter for two different geometries is also shown. The volume of a flame is empirically stated to be $\sim 0.2 \text{ m}^3/10^6 \text{ watts}^*$ or $\sim 0.0586 \text{ m}^3/10^6 \text{ Btu}$. For simplicity of calculations, a flame is usually considered to be a cylinder. However, observations tend to favor a truncated cone or frustrum. A frustrum

*Lucas, D. M. and Toth, H. E., "The Calculation of Heat Transfer in the Fire Tubes of Shell Boilers"; Journal of the Institute of Fuel; October, 1972.

TABLE 3. FLAME GEOMETRY ESTIMATION FOR BASELINE CONDITION IV

Swirl setting	Flame diameter (cm) (visual estimate)	Flame length (cm) (visual estimate)	Cylinder flame length (cm) (calculated)*,†	Frustrum flame length (cm) (calculated)*,‡
7.5	75 ± 7	16 ± 5	11 ± 2	18 ± 3
5	50 ± 7	50 ± 8	25 ± 7	43 ± 12
2.5	42 ± 7	66 ± 8	37 ± 12	63 ± 20

*Volume = $(0.2 \text{ m}^3/10^6 \text{ watts})(0.29307 \text{ watts/Btu/hr})(0.8 \times 10^6 \text{ Btu/hr})$
 $= 0.0469 \text{ m}^3$

†Length = $4V/\pi D^2$, where D = flame diameter

‡Length = $48V/7\pi D^2$, for $D_1 = 2D_2$

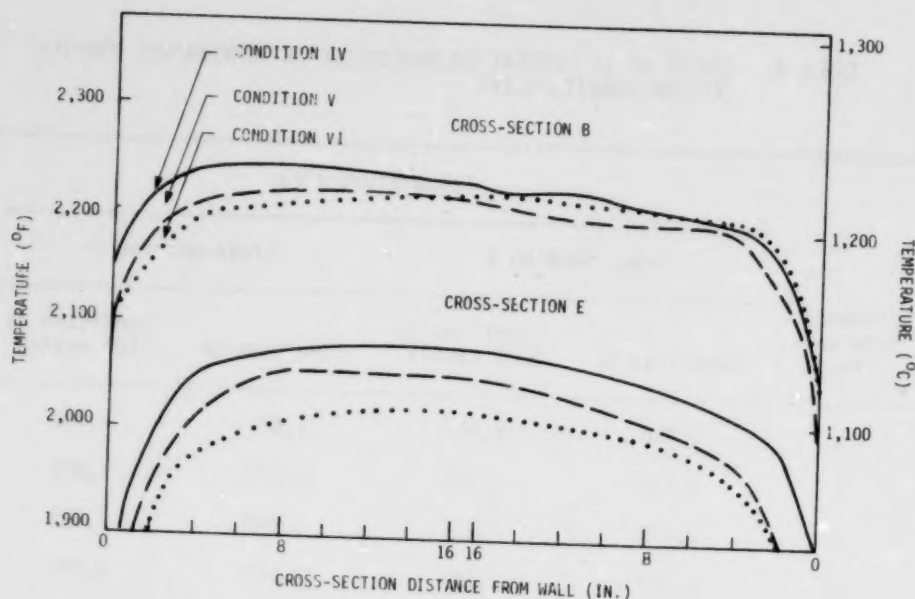


Figure 6. Effects of burner swirl setting on temperature profiles (0.8×10^6 Btu/hr and 25 percent excess air).

with $D_1 = 2D_2$ fits our observed flame lengths quite well.

Swirl settings for this burner can range from 0 to 8. The swirl settings of 7.5 (condition IV), 5.0 (condition V), and 2.5 (condition VI) represent a short, bushy flame, an intermediate flame, and a long thin flame, respectively. From the observed profiles in Figure 6, the effect of swirl is to steepen the temperature gradient as one goes to higher settings (shorter flames). However, the overall profiles range $\pm 25^\circ\text{F}$ at the centerline, or marginally outside measurement error range.

The intuitively expected results would include a reversal of the order of the temperature profiles if, indeed, the thermal gradient does change. That is, the firing condition giving the higher temperature profile at the front of the fire box should give the lower profile at the rear of the box. This considers only the bulk heat content of the gases and does not take into account changes that may arise from changes in the mass flowrates due to the shorter length of heat release. Modeling of this

phenomenon has not been completed at this time.

Effect of Waste on Temperature Profile

For baseline condition IV (nominal 0.8×10^6 Btu/hr heat input, 25 percent excess air, and swirl setting of 7.5), the effect of adding 10 percent v/v chlorobenzene in the fuel appears to be less than the noise of the various measurements (see Table 4). The heat content of the fuel is 135,000 Btu/gal while for chlorobenzene it is 112,000 Btu/gal. A 10 percent v/v mixture will have a heat content of 133,180 Btu/gal, representing a 1.7 percent decrease in the rate of heat input. The accuracy of preparing the mixture is ± 4 percent while the accuracy of the feedrate is ± 5 percent. The precision of the temperature measurements is $\pm 20^\circ\text{F}$ for points near the walls and $\pm 10^\circ\text{F}$ for points in the bulk gas. The conclusion is that the chlorine radical is not measurably changing the thermal profile beyond the flame zone.

TABLE 4. EFFECT OF 10 PERCENT CHLOROBENZENE ON TEMPERATURE PROFILE
(FIRING CONDITION IV)

Distance from wall (in.)	Temperature (°F)			
	Cross-section B		Cross-section D	
	Condition IV	Condition IV (10% waste)	Condition IV	Condition IV (10% waste)
0	1,968	2,027	1,680	1,781
1	2,113	2,120	1,823	1,870
2	2,135	2,135	1,946	1,969
3	2,172	2,168	2,019	2,002
4	2,194	2,185	2,041	2,045
8	2,186	2,189	2,064	2,060
12	2,199	2,205	2,095	2,102

Effects of Waterwalls on Temperature Profiles

Addition of waterwall panels replaces about 8 percent of the refractory surface area. The waterwalls are approximately 6 in. wide and run the length of the furnace on either side. The total surface area of the waterwall is 8 ft². The two waterwalls are each composed of three panels. The panels are individually supplied with water, and the inlet and outlet temperatures are monitored. The total water flowrate is also measured. The walls extract approximately 400,000 Btu/hr from the furnace.

An example of the effect of the waterwall on longitudinal temperature is shown in Figure 7. Not only does the waterwall lower the overall temperature profile, but it also steepens the slope. From heat flow calculations the surface temperature of the walls is estimated to be 77°C (170°F). This correlates with the observed condensation on the rear panels, the implication being that the surface temperature of the panels range

from above to below the flue gas dew point (~55°C or 130°F).

Destruction Efficiencies As a Function of Operating Variables

At the time of submittal of this paper, thirteen destruction efficiency tests had been concluded. Of these, eleven were with chlorobenzene, and two were with a mixture of carbon tetrachloride, chloroform, and methylene chloride. A summary of the results is shown in Tables 5 and 6. The relative effects are displayed in Figures 8 and 9.

It is readily apparent that the effect of the waterwalls is to decrease the destruction efficiency by 1.5 to 2 orders of magnitude. Whether this effect is caused primarily by flame cooling or by cooling of the thermal oxidation environment is not known at this time. It is postulated that the primary effect is from the latter based on the (unsubstantiated) assumption that only 90 to 99 percent of the destruction occurs within the flame. Other

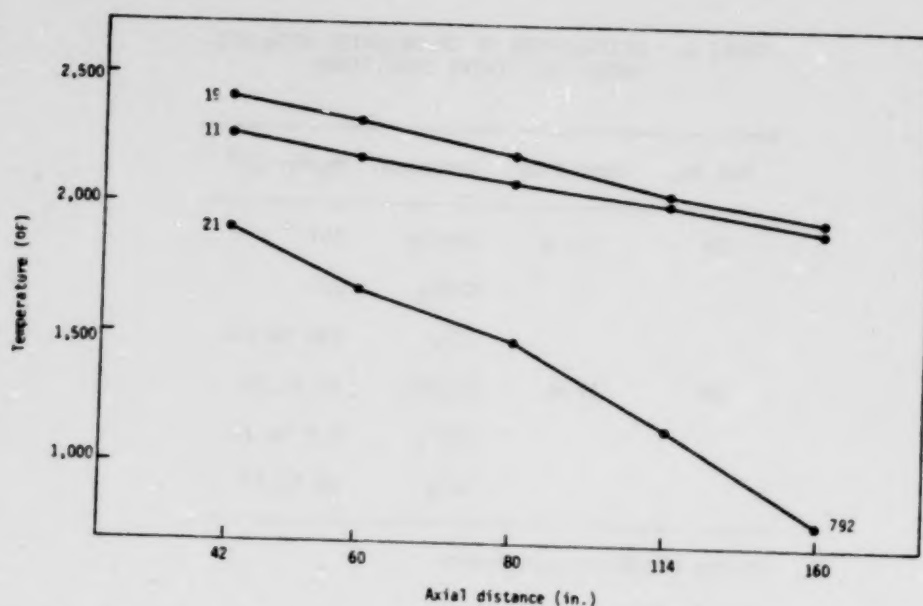


Figure 7. Changes in temperature profiles with (run 21) and without waterwalls (runs 11 and 19) for condition IV, (0.8×10^6 Btu/hr, 25 percent excess air). Runs 11 and 19 were performed 1 month apart.

TABLE 5. DESTRUCTION OF CHLOROBENZENE UNDER VARIOUS OPERATING CONDITIONS

Run no.	Condition	lb/hr In	lb/hr Out $\times 10^6$	$M_0/M_1^* \times 10^7$
12	I	6.2	1.2 to 1.6	1.9 to 2.6
14	II	5.9	0.10 to 0.52	0.17 to 0.89
23	II W†	7.0	14 to 50	20 to 72
20	III	4.0	0.2 to 1.7	0.5 to 4.2
22	III W	2.3	6.9 to 27	30 to 140
11	IV	4.6	1.7 to 2.3	3.8 to 5.1
19	IV	4.0	1.0 to 10	2.6 to 26
21	IV W	2.7	>76 to >180	>280 to >670
16	45%‡	3.9	0.18 to 0.87	0.5 to 2.2
10	45%	4.4	0.4 to 2.2	1 to 5

*Range of three test points

†With waterwalls

‡45 percent excess air rate and 0.8 million Btu/hr

TABLE 6. DESTRUCTION OF CHLORINATED METHANES
UNDER TWO FIRING CONDITIONS

Run no.	Condition	Compound	$M_0/M_1 \times 10^6$
25	III W	CH_2Cl_2	25†
		CHCl_3	22†
		CCl_4	140 to 175
24	IV W	CH_2Cl_2	52 to 74
		CHCl_3	4.9 to 15
		CCl_4	10 to 47

*Range of three test points

†Single point

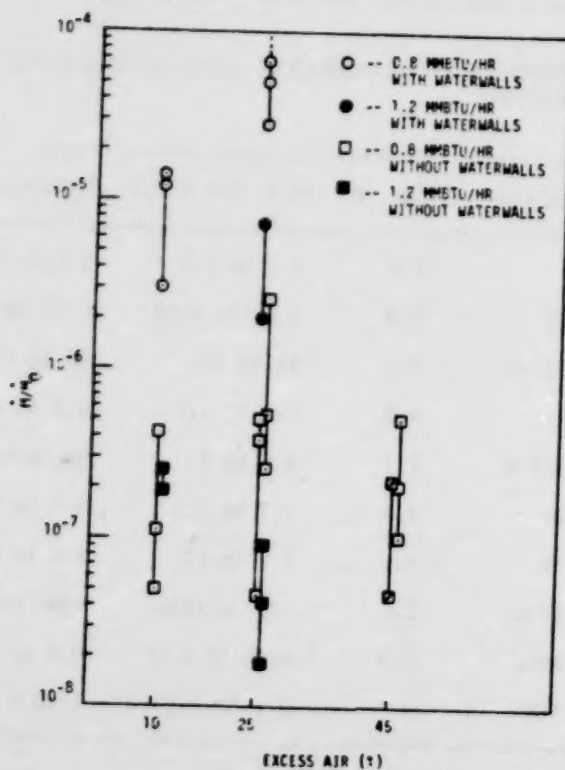


Figure 8. Chlorobenzene breakthrough versus excess air.

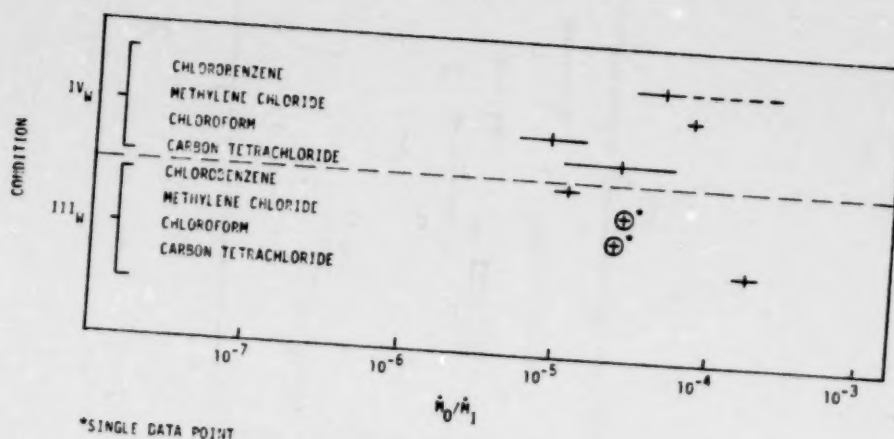


Figure 9. Relative destruction efficiencies under two firing conditions (chlorobenzene data from runs 21 and 22. Data for chloromethanes from runs 24 and 25).

correlation with operating parameters may be present, but insufficient data is available at this time. The majority of data at this time has been taken without waterwalls which pushes the detection limits (Ca 1-10 ng/trap). Thus the error associated with calculating destruction efficiencies (sampling and analytical measurements) blurs smaller effects. Comparisons of chlorobenzene breakthrough versus excess air rate is shown in Figure 10.

Comparison of Chlorobenzene Breakthrough to NO Emissions and Temperature

Plots of chlorobenzene breakthrough versus NO emissions and temperature at one point are shown in Figures 10 and 11. Although no absolute correlation can be discerned for the NO plot, it appears that an upper bound on breakthrough may be present. The upper bound behaves or would be expected from theory. That is, because NO_x production is proportional to temperature, and breakthrough is inversely proportional to temperature, as NO_x increases, breakthrough should decrease. This is what is observed. The relationship of breakthrough to temperature is

more clearly seen in Figure 11. Again, this does not reflect the true situation because it does not correlate the true spatio-temporal temperature history to breakthrough. Further data interpretation is underway to look at these aspects in more detail.

Future Efforts

Additional testing by sampling in the firebox is projected. Both centerline and boundary layer sampling will be done. In addition, coal, gas, and residual oil will be used as fuels. Finally, alternate injection methods including multiple burners and centerline injection is postulated.

Conclusions

A subscale test bed for studying the thermal destruction of organic materials as a function of boiler operating parameters has been established and characterized. Ten baseline operating conditions have been studied covering changes in firing rate, excess air rate, and burner swirl settings. Destruction efficiency tests for chlorobenzene are

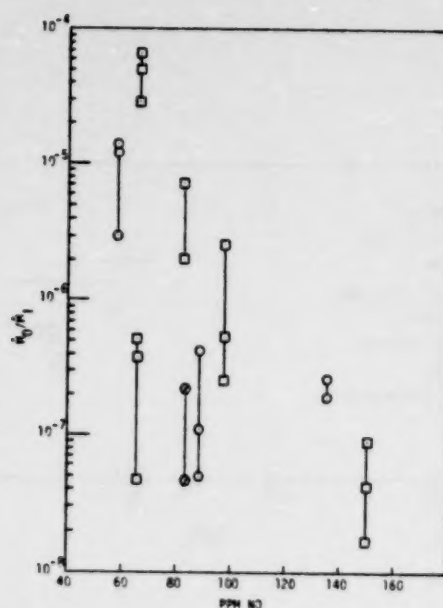


Figure 10. Chlorobenzene breakthrough versus NO emissions.

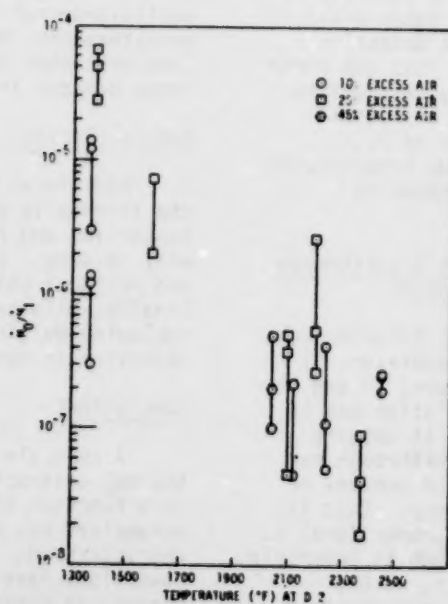


Figure 11. Chlorobenzene breakthrough versus centerline temperature at cross section D-2.

TABLE 7. ACUREX PILOT-SCALE RESEARCH FURNACE CAPABILITIES

Combustion Chamber	• 33 in. I.D. x 10 ft long • 2- and 3-ft sections • Viewports • 2-in. diameter access ports for sampling or air staging • Refractory lined (3,000°F) • Optional cooling surface • Coal-fired 1 to 1.5 million Btu/hr • Gas-fired 2.5 million Btu/hr • Oil or COM 2 million • Horizontal orientation
Convective Section	• Removable heat exchange sections -- tailor flue temperature profile • Water cooled
Air Supply	• Preheated to 600°F • Nominal 8 psi supply • Optional 125 psi supply • Up to 150 percent excess air • Measurement and control of airflow
Burner	• Variable swirl research burner -- Multiple fuel capability -- Variable axial fuel tube placement -- Capability to change velocity -- Capability to change quarl design • Capability for multiple burner design
Flue	• I.D. fan • Baghouse • Potential for flue gas recirculation

being conducted. Preliminary results indicate the potential to predict the thermal environment and possibly an upper limit on destruction efficiency.

EXPERIMENTAL

Pilot-Scale Furnace

The furnace facility is shown schematically in Figure 1 with capabilities listed in Table 7. The main combustion firebox is a horizontal, refractory-lined, cylindrical tunnel, 33 inches in diameter and 12 feet in length. The firebox can accommodate a set of stainless steel water-cooled panels to simulate gas temperatures in a watertube boiler. At the firebox exit is a

10-foot vertical convective cooling section where U-shaped watertube bundles extract heat from the burnt gases. An induced draft fan and damper at the 15-foot stack allow precise variation of firebox pressure.

The burner is mounted on the front wall of the furnace. It can be manually adjusted to operate over a large-angle of swirl geometries. The axial position of the fuel injection tube can be varied within a water-cooled quarl to ensure flame stability. Fuel oil is injected through a Delavan pressure-atomizing, hollow-cone spray nozzle.

Fuel/Air Monitoring

Liquid fuel flow is measured to ± 2 percent absolute accuracy via a Fischer & Porter rotameter. Most of the uncertainty is associated with viscosity changes in the oil as the temperature rises. Viscosity/temperature relationships for the fuel used were supplied by Truesdail Laboratories, Los Angeles, California. A large fraction of the fuel is recirculated to the fuel supply drums. The balance is pumped through the fuel tank. The oil-pressure behind the nozzle, calibrated against diesel oil volume flowrates, gives an independent verification of the firing rate. Agreement between pressure gauge and rotameter is generally better than 3 percent.

Diesel oil/chlorobenzene mixtures are prepared in 50-gallon quantities in steam-cleaned drums. Diesel oil volume is measured by a Neptune "Red Seal" Model no. 137, positive displacement totalizing flowmeter to ± 1 percent accuracy. Chlorobenzene is hand-pumped through a Tuthill "Fill-Rite" Model no. 800A totalizing flowmeter to ± 2 percent accuracy. The mixture is recirculated through the fuel feed system for 1 hour to ensure adequate mixing.

Airflow is monitored continuously by a hot-wire anemometer mounted in a venturi tube. The air is preheated to 350°F to produce entrance velocities characteristic of full-scale oil-fired furnaces.

A stainless steel probe downstream of the convective section extracts gas samples for online major species analysis. The samples are cooled, dried, and sent to an emissions bench where electro-optical analyzers determine the levels of CO₂, O₂, CO, NO_x, and unburned hydrocarbons. CO₂ and O₂ concentrations give a second verification of input stoichiometry. Airflow measurement and flue gas CO₂ determination of excess air levels agree within 4 percent.

Temperature Measurement

Since a steady-state thermal condition requires several days of furnace operation, temperature data must be collected during transient operation.

To ensure repeatable temperature (and hence destruction efficiency) data, the furnace is fixed on natural gas for 12 hours overnight. The gas firing rate is fixed at 0.7 million Btu/hr and the stoichiometry at 50 percent excess air. The time is adequate for the furnace gas and walls to cool down to temperatures repeatable within $\pm 50^\circ$. The appropriate fuel oil conditions are set the following morning, and oil is fired for 3 hours ± 15 minutes. Using this approach, temperature data are not biased by position on the heat-up curve.

During oil-firing, 12 key furnace wall and flue gas temperatures are monitored by Chromel/Alumel thermocouples. Traverses with a ceramic-sheathed platinum/platinum-10-percent Rhodium thermocouple provide gas phase axial and radial profiles in the firebox. Thermocouple radiation losses are accounted for by calibration against a section pyrometer.

Organic Sample Collection

Samples for organic analysis are collected in the flue gas duct between the convective heat recovery section and the induced draft exhaust fan. Duct gas temperatures are nominally 150°C (approximately 300°F). The sampling train consisted of a 1/4-in. SS probe, a Teflon heat traced sample line, a Tenax trap (1.5 x 12 mm containing approximately 1.5g Tenax) cooled in an ice bath, a dry knock-out trap, a wet impinger containing 0.1N NaOH solution, a silica gel impinger, a diaphragm pump, and a calibrated rotameter. The gas temperature from the Tenax trap is monitored, and sampling rates are 200 ml/min for 10 to 20 minutes. The specific retention volume for chlorobenzene on Tenax at 120°C is given as 2.3 m³ (A. D. Little, Characterization of Sorbent Resins for Use in Environmental Sampling, U.S. Department of Commerce PB 284 347, March 1978, p. 22).

Organic Sample Analysis

Tenax tubes are desorbed in a reverse direction at 200°C with approximately 100 ml N₂ onto a 1 percent SP-1000 carbopak B 60/80 mesh gas chromatographic column held at 60°C. Following the thermal desorption of the

trap the temperature is ramped 20°C/min to 220°C and held for 20 minutes the detector is a Hall electrolytic conductivity detector set in the halogen mode.

The detection limit of the method is 0.1 ng per Tenax trap. Excellent reproducibility (RSD of 6.5 percent) was obtained at concentrations of 100 ng chlorobenzene spiked directly onto the Tenax trap. The recovery averaged 92 percent at 100 ng, 85 percent at 10 ng per trap and 70 percent at 1.0 ng spiked onto the Tenax trap and desorbed as indicated above. The detector response was found to be linear in the range of 1 to 100 ng range. Reproducibility of retention time was ± 0.1 percent for a series of five traps spiked with chlorobenzene at 1 to 100 ng, analyzed sequentially.

ACKNOWLEDGMENTS

This work was performed under EPA Contract no. 68-02-3176; Task 31. The Project Officer is George Huffman. Sampling was conducted by M. Murray while analytical work was carried out under the supervision of Dr. V. Lopez-Avila. Technicians contributing significantly to the effort were R. Grose and W. G. Hellier. Critical technical input was given by Dr. L. Waterland of Acurex Corporation and members of the IRB staff. A special note of appreciation goes to the Acurex technical publications staff.

EVALUATION of HAZARDOUS WASTE INCINERATION
in a CEMENT KILN at SAN JUAN CEMENT COMPANY

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INTRODUCTION

An attractive alternative to hazardous waste incineration which makes use of a waste's heat content is cofiring of hazardous waste in high temperature industrial processes. Many such processes, which include cement and dolomite kilns, glass furnaces, steel furnaces, and some industrial boilers, provide conditions of temperature and residence time similar to those required for dedicated hazardous waste incinerators. In addition to savings derived from the heat value, the use of an existing industrial process requires less capital to process a given amount of hazardous waste than does a new incinerator.

Because of their large process capacities and energy use, cement kilns, in particular, appeared to be an excellent example of this concept. They typically operate at temperatures over 1,260°C (2,300°F), gas residence times are in excess of 1.5 seconds at or above this temperature, and the combustion zone is highly turbulent. The alkaline environment in a cement kiln absorbs acid gases such as hydrogen chloride (HCl), and the need for exhaust gas scrubbing systems is eliminated.

Because of the need to gather more data on cement kiln incineration of hazardous waste, the Environmental Protection

Agency (EPA) Industrial Environmental Research Laboratory-Cincinnati conducted a comprehensive demonstration program at the San Juan Cement Company in Dorado, Puerto Rico, from October 1981 until February 1982. The purpose of the demonstration program was to evaluate the ability of a cement kiln to destroy wastes, to generate data for the purpose of formulating permitting criteria, and to evaluate a kiln's ability to remove the HCl combustion product. A sampling program was conducted during the burning of hazardous waste. The primary goal of the program was to evaluate the effects of various waste parameters on the destruction efficiency of Principal Organic Hazardous Components (POHCs), and the change in emissions of particulate matter, hydrocarbons, carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), and hydrogen chloride (HCl). Secondary objectives were to detect and quantify the Products of Incomplete Combustion (PICs), chlorinated dibenzofurans, chlorinated dibenzodioxins, trace metals, and heavy organics.

A number of cement plants have been used to test cofiring of hazardous wastes, e.g., St. Lawrence Cement Company in Mississauga, Ontario, in 1974-1976; Peerless Cement Company in Detroit, Michigan, in 1976; Stora Vika Cement Plant near Stockholm, Sweden, in 1978; and Marquette Cement in Oglesby, Illinois, in 1981. The

data from these tests indicated that cement kilns, when properly operated, could destroy many of the organic chemical compounds in the wastes burned under the operating conditions of these tests.

A need remained within EPA for criteria to be used in deciding whether or not to regulate cement plants that burn wastes, particularly those including highly chlorinated hydrocarbons.

The facility at the San Juan Cement Company was chosen for the test because of its availability, the willingness of the company to cooperate with the Puerto Rico Environmental Quality Board (PRJCA) and U.S. EPA Region II in obtaining permits, and the suitability of the facility for a test.

Facility and Process Description

San Juan Cement Company has operated a cement plant in Barrio Espinosa in Dorado, Puerto Rico, since 1970. The location of the plant is about 27 kilometers (km) west of San Juan. The plant is dedicated to the manufacture of portland cement. Annual production averages 4.082×10^6 kilograms (kg) (450,000 tons) per year and the plant employs 350 workers; it is the second largest cement plant in Puerto Rico.

A cement kiln is the heart of the cement process, as depicted in Figure 1. A cement kiln is a large steel horizontal tube with refractory linings. Such kilns may be up to 7.6 meters (m) in diameter and over 232 m long; at San Juan Cement, kiln #2 is 137 m (450 feet) long with an outer shell diameter of 3.05 m (10 ft) and 0.305 m (12-inch) thick walls. The kiln rotates slowly (75 rotations per hour) and has a gentle slope (0.3 m/10 m length) to allow material to pass through by gravity. Cement kilns operate countercurrently; i.e., solid materials travel in one direction and hot gases plus dust emissions travel in the opposite direction. A slurry of 30% to 40% water (typically 35% to 39%) and finely crushed rock is fed into the kiln at the upper end; at the opposite end of the kiln is a powerful oil fire. At San Juan Cement kiln #2, No. 6 fuel oil is burned at about 1.51×10^{-3} m³/s (24 gpm), a heat input of

approximately 62×10^6 watts (212 million Btu/hr). As the raw material passes slowly through the kiln (1 to 4 hours), it dries; then, at a temperature of 550°C (1,020°F), calcination starts (CO₂ is extracted from the calcium carbonate in the feed); finally, it approaches the hot burning zone of the kiln. In the burning zone, 1,500°C (2,700°F) temperatures calcine and fuse the raw materials creating a complex calcium silicate aluminoferrite mineral substance called "clinker," which is discharged from the lower end of the kiln and cooled by large fans in the clinker cooler [1]. The clinker production rate at this plant ranged from 28 to 33 metric tons/hr (31 to 36 ton/hr). The addition of about 6% gypsum to milled clinker completes the process in the production of portland cement.

Exhaust gases from kiln #2 pass through a baghouse-type dust collector where entrained particulate matter is removed. The cleaned exhaust gases are then released to the atmosphere through a single stack. The baghouse employed at kiln #2 consists of 1,536 fabric filters, each 9.3 m in length. The efficiency of the baghouse in removing particulate matter from the gas stream was reported to be 99.8 percent. It was not an objective of this program to determine the baghouse collection efficiency.

Environmental Design

The sampling and analytical program was designed to identify all major pollutants from the burning of the hazardous wastes available for this program and to quantify their respective emission rates, investigate the chlorine material balance of the cement process, determine burning rate limits as related to product acceptability and refractory lining integrity, and determine the destruction and removal efficiencies (DREs) of the principal organic hazardous constituents (POHCs) in the waste fuels. The POHCs chosen for this program were the three chlorinated compounds known to be present in the waste fuel mixture:

- (1) Methylene chloride (dichloromethane), CH₂Cl₂; higher heating value (HHV) = 3058 Btu/lb

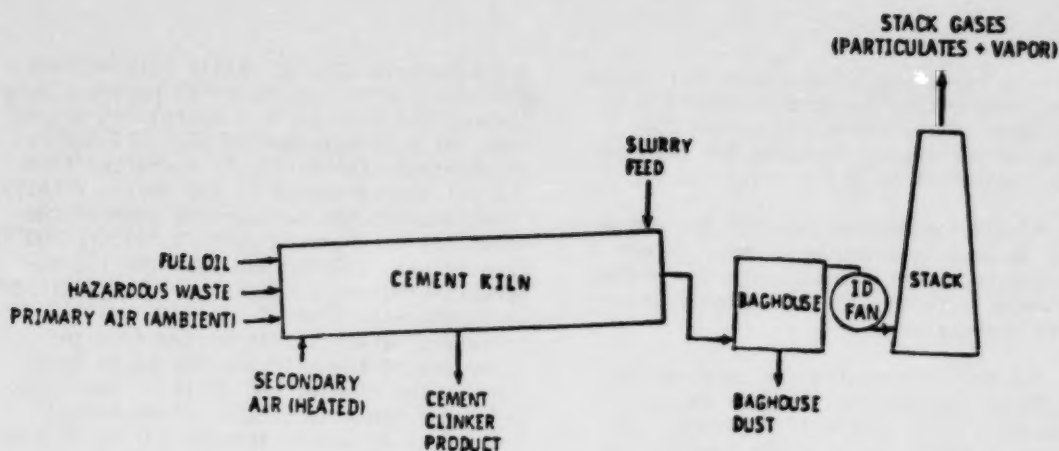


Figure 1. Schematic diagram of cement kiln burning hazardous waste.

Inputs

- fuel oil
- hazardous waste
- slurry feed

Outputs

- clinker product
- baghouse dust
- stack emissions, including
 - particulates
 - HCl vapor
 - unburned chlorinated hydrocarbons

(2) Chloroform (trichloromethane), CHCl_3 ; HHV = 1349 Btu/lb

(3) Carbon tetrachloride (tetrachloromethane), CCl_4 ; HHV = 432 Btu/lb

Emission measurements included particulate matter, carbon monoxide, carbon dioxide (CO_2), sulfur dioxide, nitrogen oxides, hydrogen chloride, total gaseous hydrocarbons (THC), total chlorinated hydrocarbons, methylene chloride, chloroform, carbon tetrachloride, trace metals in particulate matter, and organics with special attention given to dioxins and furans in the baghouse flyash. Chlorine content of the baghouse flyash and cement clinker also was monitored. The waste fuels and fuel oil used to fire the cement kiln were analyzed for principal organics, trace metals, ash, chlorine, nitrogen, and sulfur content.

Table 1 summarizes the test matrix of the demonstration program wherein the

waste feed rate to the kiln and the chlorine content of the waste were varied.

Table 2 summarizes the overall test program and shows each collection method and analytical method. A Quality Assurance Project Plan was prepared and reviewed prior to the program. A full description of the quality assurance/quality control (QA/QC) results involving replicates, splits, blanks, spikes, and reference standards is provided in the report final.

RESULTS AND DISCUSSION

A detailed summary of the waste fuel composition of each of the six waste batch shipments is given in Table 3. A seventh waste batch was burned and tested; it was a mixture of Batches 4 and 6.

Five comprehensive baseline tests (no waste fuel burned) were completed in order to determine the difference in emissions when waste fuel was burned and when it was

TABLE 1. TEST MATRIX OF WASTE FEED RATE AND CHLORINE CONTENT

Approximate waste feed rate to kiln, m ³ /s (gpm)	Chlorine in waste, wt %						
	6.5	10.1	18.7	21.4	22.9	32.0	35.1
8.39 x 10 ⁻⁵ (1.33)		x					
9.46 x 10 ⁻⁵ (1.50)	x		x				
1.10 x 10 ⁻⁴ (1.75)			x				x
1.26 x 10 ⁻⁴ (2.00)		x		x			
1.89 x 10 ⁻⁴ (3.00)						x	
2.21 x 10 ⁻⁴ (3.50)		x		x			x
2.71 x 10 ⁻⁴ (4.30)				x			
3.15 x 10 ⁻⁴ (5.00)							
3.47 x 10 ⁻⁴ (5.50)		x			x	x	
3.79 x 10 ⁻⁴ (6.00)		x					

x = Conditions tested.

not burned. Four of the baseline testing days involved EPA Method 5 testing, and the fifth test was a SASS run. The SASS was used to identify PICs and quantify dioxins and dibenzofurans.

When waste fuel was burned, ten comprehensive tests on seven different waste fuel batches were completed. These included SASS runs on waste batch numbers 3, 4, and 6; and EPA Method 5 runs on seven waste fuel burn tests. POHC testing and CO monitoring were conducted on fourteen additional tests.

Measurements of several conventional pollutants were made repeatedly during the program to determine the difference in emissions between baseline operation (no hazardous waste fed to the kiln) and waste fuel burns. Table 4 presents the comparisons for particulate, NO_x, SO₂, total hydrocarbon, and HCl emissions using the t-test to determine statistically significant difference.

In each case, pollutant concentrations were used rather than emission rates because the volumetric flowrate varied as much as 30%, and hence added another variable to the statistical analysis.

High carbon monoxide emissions are an indicator of incomplete combustion in the cement kiln. When the kiln combustion was stable, CO emission levels stayed below 10 ppm. However, any process fluctuations or change in kiln variables caused a momentary excursion in CO emissions to levels greater than 1,000 ppm (0.1%), even during baseline testing.

Figure 2 illustrates the approximately one-hour transition period and the change in CO emissions resulting from the introduction and burning of waste fuel in a kiln. From 0800 hours to 0905 hours, the kiln was not burning waste fuel, and CO emission levels hovered at 0 to 40 ppm, indicative of stable kiln operation. As the waste fuel was introduced, the CO

TABLE 2. SAN JUAN CEMENT COMPANY WASTE FUEL DEMONSTRATION
BURN SAMPLING AND ANALYTICAL PROGRAM

Parameter measured	Sampling method	Analytical method
<u>Stack Samples</u>		
Particulate matter	EPA Method 5	EPA Method 5
Metals on particulate	EPA Method 5	ICAP
Organics on particulate	EPA Method 5	Extractions and GC/MS for principal organics, dioxins, and furans
Opacity	EPA Method 9	EPA Method 9 (on site)
Sulfur dioxide	EPA Method 6	EPA Method 6
Nitrogen oxides	EPA Method 7	EPA Method 7
Carbon monoxide	EPA Method 10	NDIR continuous analyzer
CO ₂ and O ₂	Integrated bag sample	EPA Method 3 (on site)
Hydrogen chloride	Impinger train	Specific ion electrode
Total gaseous hydrocarbons	Direct to analyzer	Continuous FID
Total chlorinated hydrocarbons	Integrated bag samples	GC/EC (on site)
Three chlorinated species (POHCs)	Integrated bag samples	GC/EC (on site)
Organic compound speciation	SASS train	GC/MS
<u>Ambient Air</u>		
Particulate matter	High volume gas sampler	EPA-Appendix B FR 121:0105
<u>Process Water</u>		
Organics (3 species)	Integrated sample	EPA priority pollutant methodology, GC/MS
<u>No. 6 Fuel Oil</u>		
Btu content	Grab	ASTM D240-64
Chlorinated methanes	Grab	GC/EC
Sulfur content	Grab	ASTM D-3177
Trace metals	Grab	ICAP
Principal organics	Grab	GC/MS
<u>Waste fuel</u>		
Btu content	Grab	ASTM D240-64
Moisture content	Grab	GC/MS
Total chlorine	Grab	ASTM D8081
Total nitrogen	Grab	Kjeldahl
Total sulfur	Grab	ASTM D129
Trace metals	Grab	ICAP
Principal organics	Grab	GC/MS
PCBs and pesticides	Grab	GC/MS and GC/EC
Ash content	Grab	ASTM D482-IP4
<u>Solid Waste (kiln dust)</u>		
Principal organics	Grab	Extraction and GC/MS
Furans and dioxins	Grab	ASTM D-808
Chlorine content	Grab	ASTM D-808
E.P. toxicity	Grab	Extraction and GC/MS
Furans and dioxins	Grab	ICAP
Trace metals	Grab	ICAP

TABLE 3. SUMMARY OF WASTE FUEL ANALYSES FOR CEMENTO
SAN JUAN DEMONSTRATION BURN (volume basis)

Compound	Batch 1, vol %	Batch 2, vol %	Batch 3, vol %	Batch 4, vol %	Batch 5, vol %	Batch 6, vol %	Batch 4/6, vol %	Density, g/ml	TLV, mg/m ³
Water	<1.0	4.1	4.3	8.9	23.0	2.0	NA	1.000	- ^d
Methanol	10.4	7.1	13.9	6.2	10.9	ND ^a	NA	0.7914	260
Ethanol	0.8	3.2	6.6	4.7	16.8	5.6	NA	0.7983	1,900
Acetone	14.2	12.2	11.2	10.5	4.6	2.2	NA	0.7899	2,400
2-Propanol	4.7	5.2	5.3	4.5	3.1	1.6	NA	0.7855	500
Methylene chloride (POMC)	24.4	16.9	12.0	12.1	1.4	5.0	5.1	1.3266	360
Hexane isomers	3.9	3.2	1.8	1.5	ND	1.5	NA	0.6532	- ^d
3-Methylpentane	5.4	4.6	2.7	3.2	ND	3.6	NA	0.6445	- ^d
Hexane	19.8	17.3	7.2	8.5	5.9	15.7	NA	0.6603	1,800
Chloroform (POMC)	1.0	0.8	3.4	5.4	4.0	0.1	0.9	1.4832	50 ^f
Ethyl acetate	4.0	14.0 ^b	9.0	6.6	3.5	22.7	NA	0.9003	1,400
Carbon tetrachloride (POMC)	ND	NA	0.4	<1.0	ND	ND	NA	0.9130	610 ^f
Benzene	0.8	0.6	1.4	10.2	7.8	0.01	1.5	1.5940	35 ^f
Hexamethyl disiloxane	0.4	0.4	0.2	0.3	0.1	0.05	NA	0.8787	35 ^f
Toluene	0.1	ND	ND	<0.5	NA	NA	NA	0.8723	- ^d
Acrylonitrile	0.2	0.1	0.02	NA	ND	NA	NA	0.8669	375 ^f
Methyl ethyl ketone	ND	1.0	1.1	<0.7	1.0	ND	NA	0.8060	5 ^f
C ₆ -benzene isomer	NA	NA	0.08	1.1	NA	NA	NA	0.8054	590 ^d
C ₆ -benzene isomer	NA	NA	1.33	0.5	0.9	2.2	NA	0.90 ^e	- ^d
Sec-butyl ethylbenzene	NA	NA	ND	NA	ND	23.8	NA	0.90 ^e	- ^d
Xylene isomers	NA	NA	1.23	1.7	NA	NA	NA	0.90 ^e	- ^d
Diallylphenol isomer	NA	NA	0.24	NA	NA	ND	NA	0.87 ^e	435 ^d
1,1'-(1,2-ethanediol)bis-	NA	NA	0.04	NA	ND	ND	NA	0.90 ^e	- ^d
4-methoxybenzene	NA	NA	0.23	NA	NA	NA	NA	0.90 ^e	- ^d
Unknowns	NA	9.3	14.3	11.9	17.9	13.9	NA	0.90 ^e	- ^d
PCBs, ppm ^g	<50	<100	<100	<100	<100	<100	<100		
Pesticides ^h , ppm	<100	<100	<100	<100	<100	<100	<100		
Properties									
Btu content, Btu/lb	11,186	11,198	11,022	10,999	4,546	13,098	NA		
Specific gravity	NA	NA	0.9948	0.9885	1.0092	0.9163	0.9410		
Chlorine content, wt %	32.0	22.9	21.4	35.1	10.7	6.5	10.1		
Ash content, wt %	0.30	0.20	0.38	0.23	0.31	0.046	NA		

^aND = not detected, generally <0.1% by volume. Components were quantified in volume % because external standards were prepared on a volume basis.

^bNA = not analyzed.

^cThreshold limit value for workplace air.

^dNo TLV assigned to this compound or isomer.

^eEstimated values.

^fSuspected or known carcinogen.

^g%s per priority pollutant list.

TABLE 4. COMPARISON OF POLLUTANT LEVELS BETWEEN
NORMAL OPERATION AND WASTE FUEL FIRING IN
CEMENT KILN NO. 2, SAN JUAN CEMENT COMPANY

Pollutant	Mean loading		Statistical significance at 95% degree of certainty
	Baseline	Waste firing	
Particulate matter	93 $\pm$ 65 mg/m ³ ^a (n=4)	99 $\pm$ 65 mg/m ³ (n=7)	No significant difference
NO _x	136 $\pm$ 83 ppm (n=4)	68 $\pm$ 23 ppm (n=9)	Significant difference
SO ₂	279 $\pm$ 243 ppm (n=4)	450 $\pm$ 245 ppm (n=6)	Significant difference
Total hydrocarbons	8.3 $\pm$ 2.1 ppm (n=9)	12.7 $\pm$ 2.1 ppm (n=7)	Significant difference
HCl	0.82 mg/m ³ (n=2)	3.3 $\pm$ 1.7 mg/m ³ (n=9)	Significant difference

^a95% confidence level.

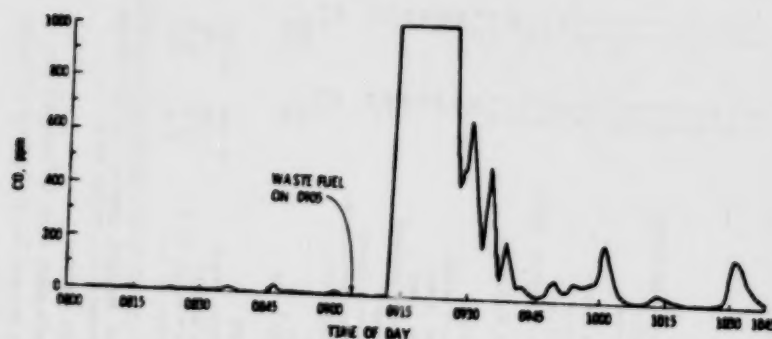


Figure 2. Illustration of waste fuel burn transition period
effect on carbon monoxide emissions, Run W6-SASS-1,
28 January 1982, San Juan Cement Company.

levels rose rapidly beyond 1,000 ppm for approximately 20 min and then returned to levels below 100 ppm as the kiln operation was stabilized.

POHC Destruction and Removal Efficiency

The complex combustion chemistry for organic materials becomes perplexing when a

broad range of organic compounds present in a liquid waste are burned. On a weight basis, most of the organic carbon in the waste is oxidized to CO_2 in the combustion process, but trace amounts of organic chemicals survive the oxidation process and are only partially reacted. In addition, small amounts of other organic chemicals must be produced if proper conditions exist. Oxidative chemical principles would suggest that all organic compounds regardless of their origin would be converted to CO_2 and other primary products if a sufficiently high temperature is achieved in the presence of adequate oxygen for a time long enough for complete oxidation to occur. If the conditions of temperature, time, and oxygen are not met, the combustion of the organic material in the fuel, plus any new organic components formed in the combustion process, would be expected to be incomplete and some possibly detrimental compounds of concern may then appear in the effluents [2]. This demonstration program investigated the amount of destruction of the organic compounds in the waste (DRE of the POHCs) and the types of organic compounds (PICs) formed.

Currently, cement kilns which burn hazardous wastes are not regulated under RCRA. However, in this study kiln performance in destroying waste was compared to that required by regulation for hazardous waste incinerators.

The destruction and removal efficiency for an incineration/air pollution control system is defined by the following equation:

$$\text{DRE} = \frac{W_{\text{in}} - W_{\text{out}}}{W_{\text{in}}} (100\%)$$

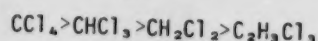
where DRE = destruction and removal efficiency, %

W_{in} = mass feed rate of the principal organic hazardous constituents (s) to the incinerator

W_{out} = mass emission rate of the principal organic hazardous constituent(s) to the atmosphere (as measured in the stack prior to discharge).

Within the family of chlorinated hydrocarbons, the monocarbon compounds are

believed to be among the most difficult to destroy thermally. The carbon-chlorine bond is especially tenacious and in general, the more C-Cl bonds present, the more difficult it will be to destroy the compound. Accordingly, a monocarbon chlorine-containing molecule will tend to be harder to destroy thermally than a two-carbon chlorine-containing molecule. The Gibbs free energy of formation values at 1600°C (2912°F) illustrate this. For the following compounds, the amount of energy required to form a molecule (conversely, the "difficulty" required to destroy it) will be greatest for carbon tetrachloride and least for trichloroethane ($\text{C}_2\text{H}_3\text{Cl}_3$).



Concentrations of the POHCs were measured during baseline testing (days when no waste fuel was burned) in order to give background or normal concentrations of these compounds in the exhaust gas. The average background level was then subtracted from the results obtained during a waste fuel burn to arrive at the contribution attributable to the waste burn.

The average DRE for the POHCs for each test run is presented in Table 5. Methylene chloride was destroyed to at least 99.0% efficiency, with the only exceptions being the two tests with waste batch #5 which contained only 1.4% methylene chloride. In general, the lower the mass feed rate of a POHC, the lower was the DRE.

Chloroform and carbon tetrachloride were more difficult to destroy than methylene chloride. Also, in most waste batches, methylene chloride was the most bountiful POHC in the waste. Waste batches #4 and #5 had the largest amounts of chloroform and carbon tetrachloride, and the best DRE results for carbon tetrachloride were observed for the test runs on these two batches. Figure 3 illustrates the frequency of obtaining a certain "number of nines" of DRE for each of the POHCs in the demonstration program. In only a few instances was the desired 99.99% or even 99.9% DRE obtained for the chlorinated monocarbon compounds chosen as POHCs in this program.

TABLE 5. DESTRUCTION AND REMOVAL EFFICIENCIES OF POHCS FOR DEMONSTRATION BURN TESTS AT SAN JUAN CEMENT COMPANY KILN #2

Run number	Methylene chloride	Chloroform	Carbon tetrachloride
W1-2 ^a	>99.997	>99.842	99.309
W2-1 ^a	99.995	>99.859	>99.996
W3-1	>99.991	99.887	91.043
W3-2	99.960	99.932	96.864
W3-3	99.659	>99.960	98.977
W4-1	98.237	98.592	97.732
W4-2	99.418	99.470	98.122
W4-3	99.461	99.283	99.142
W4-4	99.984	98.975	99.684
W4-5 ^c	99.335	99.950	99.069
W5-1 ^c	93.292	98.388	99.553
W5-2 ^c	96.663	96.099	99.460
W6-1	99.223	- ^b	- ^b
W4/6-1 ^c	99.760	95.617	94.129
W4/6-2 ^c	99.668	92.171	99.325
W4/6-3 ^c	99.564	98.703	94.512
W4/6-4 ^c	99.133	>99.737	92.253
W4/6-5 ^c	99.474	97.515	95.873

^aWaste feed rate was estimated.

^bNot present in waste fuel

^cStack gas volumetric flow rate of 1619 dscmpm used.

In one instance, run number W6-1 for CCl₄, the W_{out} exceeded the W_{in}. The mass feed rate to the kiln was less than 0.11 kg/hr. The higher mass emission rate observed suggests that CCl₄ is formed as a product of incomplete combustion from the combustion of methylene chloride and chloroform.

There are two probable reasons to explain the low DRE results obtained in the demonstration program: (1) lack of atomization of the waste fuel, and (2) difficulty of incinerability of highly chlorinated monocarbon compounds. The waste fuel injection had to match the fuel oil injection pattern in order to prevent flame impingement on the inner wall of the kiln and preignition, or backpuffing, of the fuel oil stream. Therefore, methods to increase the waste fuel atomization were not

attempted.

Other compounds were detected by gas chromatography/electron capture (GC/EC) during the analyses for POHCS, which eluted at retention times of 0.51 min (CH₂Cl₂), 0.80 min (CHCl₃), and 1.01 min (CCl₄). The most commonly seen compound had a retention time of 0.57 min to 0.61 min, which a post-test laboratory experiment with duplicate GC conditions tentatively identified as trichlorotrifluoroethane. This compound most probably was Freon 113 from the laboratory's air conditioner. Another compound which was seen in several instances eluted at about 1.1 min and was tentatively identified as trichloroethylene, a likely PIC from chloromethane combustion. 1, 1, 1-trichloroethane (1.54 min R. T.), tetrachloroethylene (1.68 min R. T.), acetone (2.11 min

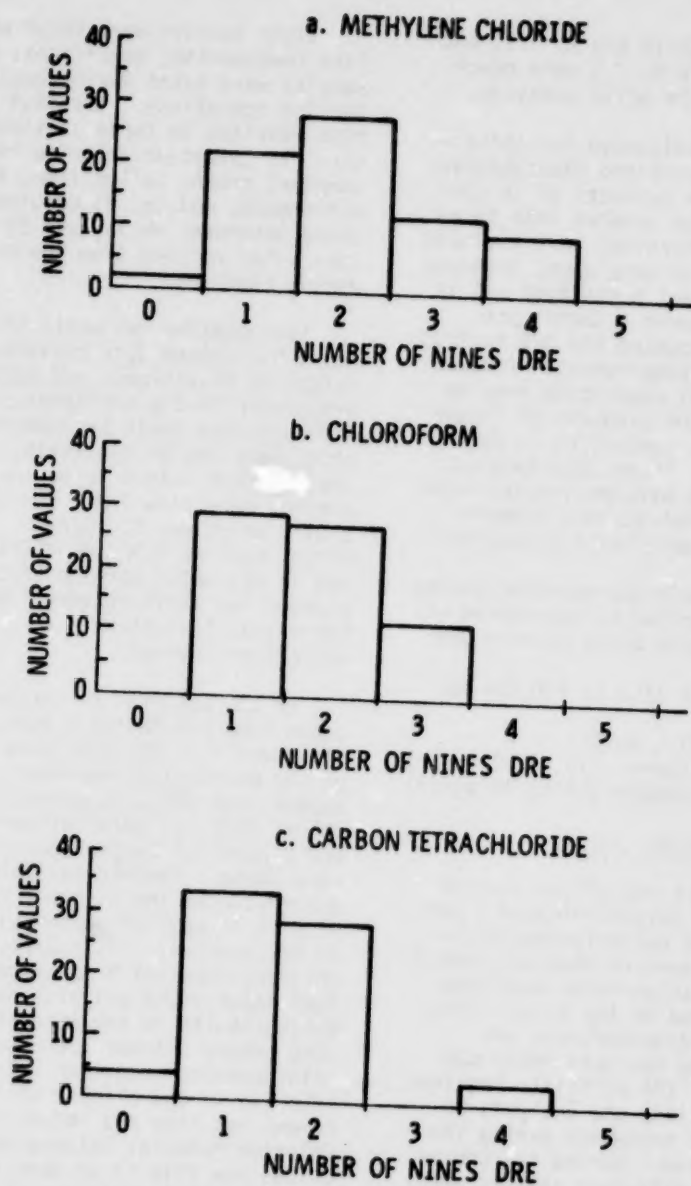


Figure 3. Frequency distribution of DRE results for each POHC.

R. T.), acetone (2.15 min R. T.), and acrylonitrile (2.16 min R. T.) were never detected by the in-field GC/EC analyses.

The SASS samples collected for chlorinated dioxins and chlorinated dibenzofurans also were analyzed for products of incomplete combustion. Four samples (one baseline and three waste burning) were analyzed for PICs. The baseline sample was analyzed because the cement plant burns fuel oil as its primary energy source. During the program, fuel oil accounted for 87% to 100% of the kiln's energy requirement. Products of incomplete fuel oil combustion need to be distinguishable from products of incomplete hazardous waste combustion -- hence the baseline sample. Three SASS samples were collected during hazardous waste burning representing different feed compositions, feed rates, and operating conditions.

The PICs which were not detected during the baseline test and can be considered attributable to hazardous waste burning are:

- Trichloroethylene (100 to 100,000 mg/hr)
- Phenol (2.4 to 11.0 mg/hr)
- C₂-naphthalene isomers (10 to 50 mg/hr)
- C₃-naphthalene isomers (14 to 46 mg/hr)

Dioxin and Dibenzofuran Results

One of the objectives of the program was to determine if polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) were emitted as products of incomplete combustion while hazardous waste was being fired to the kiln. Chlorinated dioxins and dibenzofurans are believed to be among the most toxic substances to humans. EPA officials required that extensive sampling and analysis be conducted for these compounds during the demonstration program. During the course of the program, 28 different samples were collected for analyses as shown below.

- 4 SASS train samples (particulates and vapors in stack gas)
- 5 EPA Method 5 samples (particulates in stack gas)
- 11 baghouse dust samples (plant solid waste)
- 8 RCRA extracts of baghouse dust samples (plant solid waste)

Eight samples were taken during baseline (nonburning) conditions, and 20 samples were taken during hazardous waste burning operations. The SASS train samples resulted in three sections for analysis: 1) methylene chloride rinses of the sampling probe, teflon line, filter holder, and organic module, 2) combined filter and XAD-2 adsorbent resin, and 3) the condensate water removed from the organic module during sampling.

The baseline (no waste fired) SASS run (BS-SASS) showed some positive, detectable values of hexachloro- and heptachlorodibenzofuran in the adsorbent resin extract, although none could be detected in the other portions of the train. This caused the reported values to be less than the average detection limit for the entire train, which was 3.4 ng/m³. It is noteworthy that no PCDDs or PCDFs were detected in any waste burning SASS samples at a detection limit ranging from 1.6 ng/m³ for tetrachloro-isomers to 4.9 ng/m³ for octachloro-isomers.

In the analyses of the particulate catch from EPA Method 5 runs, no detectable quantities of PCDDs were found in any of the particulate samples. In only one sample, run W3-3, 11.0 ng/m³ of pentachloro-PCDF, 26 ng/m³ of hexachloro-PCDF, and 8 ng/m³ of heptachloro-PCDF isomer were found. These detectable emissions occurred when the kiln was fed 2.75 x 10⁻⁴ m³/s (4.35 gpm) of waste which contained 21.4% chlorine. This corresponds to a chlorine input of 3.5% by weight of total fuel input (fuel oil plus hazardous waste) which results in the production of off-spec cement clinker and a potentially kiln-damaging condition. Excessive chlorine in the clinker will lengthen cement set time and reduce strength. The Chlorine Material Balance section describes how this is an operating condition which is intolerable for the cement plant. Thus, the generation of detectable quantities of PCDFs occurred only when operating an "upset" or "out-of-control" kiln. Under other conditions the cement process did not emit PCDFs, and it did not emit PCDDs under any waste burning conditions. This lack of detectable quantities of PCDD and PCDF is an expected result because the waste fuel contains no poly-

chlorophenolate precursors, the combustion temperatures were typically well above 1000°C, and a supplemental fuel was used to burn the wastes [2].

Chlorine Material Balance

The combustion of chlorinated hazardous wastes as auxiliary fuel in cement kilns results in the generation of hydrogen chloride (HCl) in the kiln. Hydrogen chloride can be absorbed by the clinker product, cement kiln lining, or baghouse dust; it also may be emitted as part of the particulate. Unabsorbed HCl will be emitted from the stack as will the unburned chlorinated hydrocarbons. HCl is formed rather than chlorine gas (Cl_2) because the conversion of chlorine gas to hydrogen chloride is favored by high temperatures and high water content in the combustion gas. Typically, the burning zone temperature in a cement kiln is 1425°C (2600°F) with a moisture content of about 10% to 15%. In wet process cement kilns, additional moisture is added to the combustion gases in the slurry drying zone of the kiln. Equilibrium calculations show that 99.87% of the chlorine in the combustion gases will be present as HCl; only 0.013% of the chlorine will be present as chlorine gas. The HCl is rapidly absorbed by alkaline calcium, sodium, and potassium compounds present in the clinker and dust to form sodium, potassium, and calcium chlorides.

In addition to calcium, while it is the major element of the cement-making process, sodium and potassium are important impurities in the raw feed material. They are undesirable in the clinker and are normally removed by the addition of chloride to the kiln -- either in the form of calcium chloride or as HCl. The resultant sodium chloride (NaCl) and potassium chloride (KCl) volatilize at the temperature of the kiln, condense as a particulate in the cooler end of the kiln, and are removed by the air pollution control device. The amount of chloride that a given kiln can handle is limited by the sodium and potassium content of its feed. If excessive chlorides are added to the system, these salts can form a clinker ring in the kiln and possibly damage the refractory lining [3].

The distribution, or fate, of the chlorine (as chloride) was studied in seven tests by measuring the chlorine-chloride content of the input and output streams of the kiln. The material balance closures for chlorine ranged from 83% to 104% with an average closure of 92%.

In this study, it was found that about 82% of the chlorine fed to the cement kiln will appear in the clinker product. The amount of chlorine in the clinker is presumed to be dependent, primarily, upon feed alkalinity, and will vary from one cement plant to another. Other cement plants with different slurry feed composition and alkalinity will realize different results, e.g., up to 92% of the chlorine was retained in the clinker at St. Lawrence Cement in Mississauga, Ontario, during those tests.

Normally, the potassium contained in the slurry feed leaves the kiln as potassium sulfate (K_2SO_4) and potassium oxide and is collected in the baghouse. Presumably, HCl reacts with K_2SO_4 to form KCl salt which is trapped in the clinker. The kiln operates above the dew point for H_2SO_4 (~160°C), and H_2SO_4 not absorbed by dust will leave as a vapor increasing SO_x emissions. Earlier, it was shown that there is a "statistically significant change" in SO_x emissions when burning hazardous waste. The average SO_x emission rates may indeed be higher due to the chemistry of the inorganic elements in the kiln; i.e., the chloride acid gas is trapped (scrubbed) preferentially over the sulfate acid gas.

The amount of chlorine appearing in the stack emissions as unburned chlorinated hydrocarbons ranged from 0.076% to 4.3% which represented appropriate overall destruction and removal efficiencies of 99.924% to 95.7% on a total chlorinated hydrocarbons feed basis. The tests showed lower DREs when burning higher levels of carbon tetrachloride. The total absorption of HCl by the cement kiln process averaged 99.7% in seven tests.

The amount of chlorine appearing in the baghouse dust varies from 5% to 26% of the total chlorine feed. The amount of chlorine appearing in the baghouse dust is influenced by the concentration of chlorine in the total fuel (fuel oil plus hazardous waste).

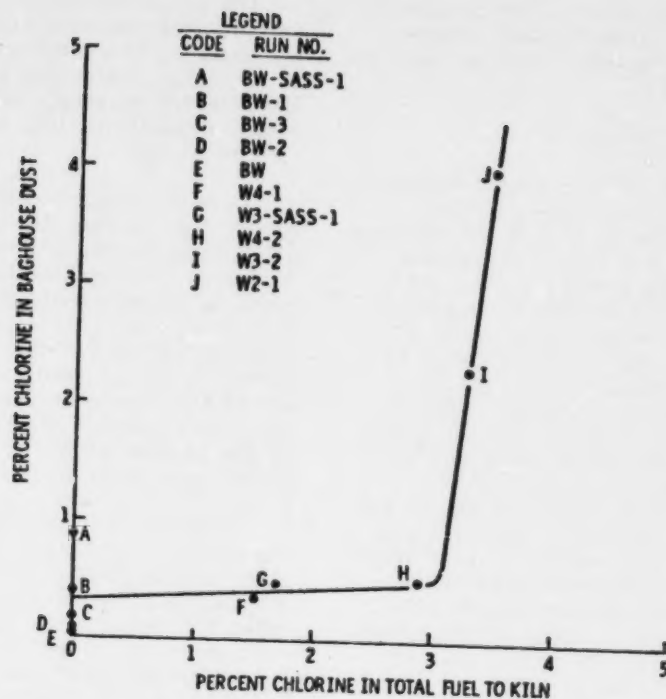


Figure 4. Effect of chlorine concentration in total fuel (fuel oil + hazardous waste) on chlorine content of baghouse dust at San Juan Cement Company.

Figure 4 shows the dramatic increase in chlorine concentration in baghouse dust when chlorine comprises 3% by weight or more of the total fuel. The plant always went into an upset condition about 90 minutes after the start of a trial burn which had 3% or more of chlorine in the total fuel. Some key observations based on the experience of saturating this kiln with chlorine are listed below.

The cement kiln will remain in a stable and controlled operating condition when the chlorine content of the total fuel (fuel oil plus hazardous waste) is 3% by weight or less. When the chlorine content exceeds 3%, the kiln becomes operationally unstable about 90 minutes after the start of burning more than 3% chlorine in the total fuel. The instability takes several forms. The burning zone temperature

drops from 1430°C (2600°F) to 815°C (1500°F) in less than two minutes some 80 to 90 minutes into the burn. The kiln starts a rapid loss of refractory lining (coating) to cement clinker product. A clinker ring forms in the burning zone. Hydrocarbon emissions increase (about fourfold) in the stack.

Recovery from this upset condition is achieved by shutting off the hazardous waste while maintaining a constant heat balance. Remarkably, the kiln recovers in 12 to 15 minutes if the waste is shut off as soon as the kiln goes into an upset condition. Continued operation during an upset would destroy the kiln. It is presumed that the excess chlorine is absorbed in the lining and reduces its slagging temperature to below 815°C (1500°F). When

the lining starts to slag, all heat is used to melt the lining, not to make cement. It is presumed that the kiln recovers in about 15 minutes because it takes the burning zone about 15 minutes to purge itself of slagged lining. Recovery is as dramatic as is the upset.

• Even though the cement kiln remains stable up to about 3% chlorine in the total fuel, the product quality becomes unacceptable when the chlorine content exceeds 1% of the total fuel at the San Juan Cement Company.

• Clinker rings can be formed by either temperature excursions in the burning zone when not burning hazardous waste or by excessive chlorine additions to the kiln. Operators at San Juan Cement Company were successful at breaking clinker rings simultaneously with burning chlorinated hazardous waste. It was not necessary to cease hazardous waste burning in order to break a clinker ring.

Incineration of hazardous wastes in cement kilns also demonstrated a time delay in the release of chlorine from the kiln. The onset of unstable kiln operations some 90 minutes after excess quantities of chlorine are added to the kiln was just described. Figure 5 shows the dynamic behavior of chlorine releases from the cement kiln compared to a constant, short duration, and a moderate, but still excessive, chlorine feed rate to the cement kiln. It can be seen that it actually takes about three hours for the kiln to completely purge itself of the added chlorine.

CONCLUSIONS

Some of the results observed in this demonstration program were contradictory to results from other cement kiln incineration tests; e.g., lower DREs, no change in particulate emissions, and significant changes in SO_2 and NO_x emissions. The conclusions presented below apply only to this particular kiln and the results from this demonstration program.

1. The inability of this kiln to consistently achieve 99.99% DRE (a value

which hazardous waste incinerators must demonstrate) of the POHCs is attributed to unatomized waste introduction to the kiln flame and the difficult incinerability of the POHCs. These compounds (CH_2Cl_2 , $CHCl_3$, and CCl_4) are occasionally employed as fire retardants because of their ability to move hydrogen atoms from the free-radical branching combustion reactions to form HCl. Combustion of chlorinated species containing less chlorine may have resulted in higher DREs.

2. Chlorinated dioxins and chlorinated dibenzofurans are not produced at detectable levels (1.6 ng/m^3) when a cement kiln firing chlorinated wastes is operating normally.

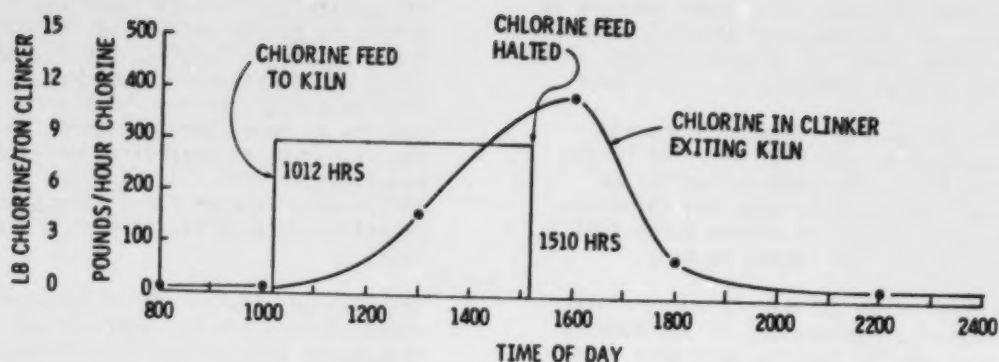
3. A cement kiln will absorb over 99% (about 99.7%) of the HCl formed during the combustion of chlorinated hazardous wastes. This absorption is partitioned between the clinker and baghouse dust.

4. At San Juan Cement Company, approximately 82% of the chlorine fed to the cement kiln appears in the clinker. This limits the chlorine content of the total fuel to less than 1%. This may vary at different cement plants because quarry alkalinity (ability to absorb chlorine) varies at each cement plant.

5. Achievable fuel savings are a function of the chlorine content of the waste and each plant's ability to absorb chlorine. At San Juan Cement Company, a hazardous waste containing less than 5% will result in at least a 20% savings in fuel costs. Higher fuel savings may be possible for higher chlorine contents at other plants.

6. Production of salable cement product is possible when burning chlorinated hazardous wastes provided the plant's chlorine absorbability limit is not exceeded.

7. Atomization of the waste fuel would be desirable, if a flame configura-



- tion can be obtained which does not alter the primary fuel flame configuration.
8. High feed line pressure [1,380 to 2,070 kPa (200 to 300 psig)] is not required for waste injection to the kiln. This pressure requirement may change depending on the type of atomizing nozzle used.
 9. There is no significant change in particulate emission due to burning chlorinated hazardous wastes. This result was observed on a cement kiln equipped with a fabric filter air pollution control system. A cement kiln with an electrostatic precipitator may not achieve similar results due to a change in dust resistivity.
 10. Emissions of sulfur dioxide, total hydrocarbons, and hydrogen chloride increased significantly when waste was burned. A cement kiln with a higher alkalinity feed than that at the San Juan Cement Company may not have an increase in SO_2 emissions.
 11. Emissions of nitrogen oxides decreased significantly when waste was burned.
 12. There is no change in particulate ambient air quality due to hazardous waste combustion in cement kilns.

13. The solid waste (baghouse dust) generated by hazardous waste burning and its RCRA extract (leachate) are suitable for land-filling.

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AUTOMATED METHODOLOGY FOR ASSESSING INHALATION EXPOSURE TO HAZARDOUS WASTE INCINERATOR EMISSIONS*

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ABSTRACT

The Inhalation Exposure Methodology (IEM) is a system of computer programs developed to estimate atmospheric transport and population exposure to airborne pollutants released from hazardous waste incinerators. This paper outlines the capabilities of IEM and discusses operation of the version installed on the IBM system at the National Computer Center, Research Triangle Park, North Carolina. Important factors affecting IEM exposure estimates are discussed. A six-site comparison shows total exposed population estimates made using two other methods to differ from IEM estimates by between -13 and +9%. Corresponding exposure estimates show differences between -36 and +35%.

INTRODUCTION

The Inhalation Exposure Methodology (IEM) was developed to provide research and regulatory offices within the U.S. Environmental Protection Agency (EPA) a means to assess the impacts of stack and fugitive emissions from hazardous waste incineration facilities. IEM is an automated set of programs and data for estimating ambient pollutant concentrations and human inhalation exposures in the vicinity of a facility. Only knowledge of the facility's physical dimensions, pollutant emission rates, location, and site climatology is required to obtain exposure estimates.

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IEM can be employed in a variety of ways. It has been used by the Office of Solid Waste to estimate total population exposures from incinerators which have measured stack emissions. It also can be used to compare the effects on population exposures of different stack pollution control requirements. Applications of these types can provide a measure of the need for and effectiveness of regulating hazardous waste incinerator emissions. In addition, because IEM uses a sophisticated air dispersion code which allows separate modeling of a number of emission sources at a given facility, the methodology has been used in comparing the relative importance of stack emissions versus fugitive emissions on nearby populations. This has allowed researchers to determine the relative significance of various emission sources and to prioritize future work.

To date, IEM has been used only to model incinerator emissions, but its capability of handling area and

volume sources as well as point source emissions should make it applicable to other hazardous waste facilities. IEM also provides the user with direct access to historical weather station data files and to a nationwide, 1980 population data base. The latter feature has been used in ground water impact studies, where there was a need to determine the number of individuals who might be exposed to leachates from lagoons or land disposal facilities.

IEM has been installed on the IBM system at the EPA's National Computer Center in Research Triangle Park, North Carolina. It may be run from remote or on-site IBM-accessible terminals. Persons wishing to use IEM should arrange access to the IBM system and IEM through their Project Officers.

The methodology consists of a system of computer programs that uses on-line meteorological and population data bases and user-supplied input data to provide various tabulations of pollutant concentrations and population exposures (O'Donnell et al., 1983). There are four groups of computer programs (Fig. 1) and several permanently stored meteorological and population data files. The MET group selects a meteorological data set from permanently stored files containing National Oceanic and Atmospheric Administration Stability Array (STAR) data, and formats it for use in the atmospheric dispersion program - a slightly modified (ISCLTM) long-term version of the Industrial Source Complex Dispersion Model (ISCLT, Bowers et al., 1979). ISCLTM uses the meteorological data and other required input to calculate average ground-level air concentrations of pollutants emitted from sources located at the site of interest. The POP group selects a site-specific population distribution from permanently stored, specially prepared,

1980 census population data and formats it for use in the concentration-exposure program (CONEX). CONEX takes the concentration estimates from ISCLTM and the population distribution from the POP group and prepares a variety of tables that allow analysis of pollutant concentrations and population exposures around the site.

The flow of program execution and data input in IEM are controlled by eight interactive executive (EXEC) routines, which must be run in proper sequence and within a span of a few days. Each EXEC routine contains appropriate job control and program statements to access system-stored data files and programs, direct the user in preparation of a problem-specific input data file, and run the program and process program outputs. The language used to control an IEM session is INTERACT (WYLBUR 6.0). Because some of the programs must be run sequentially and may have a long (greater than eight hour) turnaround, four days are typically required to make a complete IEM run on the EPA IBM system.

This paper gives an outline of the operation and capabilities of IEM. Use of IEM is detailed in its users' guide (O'Donnell et al., 1983). Several factors affecting IEM exposure estimates are also discussed. An indication of how well IEM exposure and exposed population estimates agree with estimates produced by other methods is given using pollutant concentrations at six sites in different parts of the United States.

COORDINATE SYSTEMS

IEM uses two polar coordinate systems - the "grid" system and the "centroid" system. Each system is

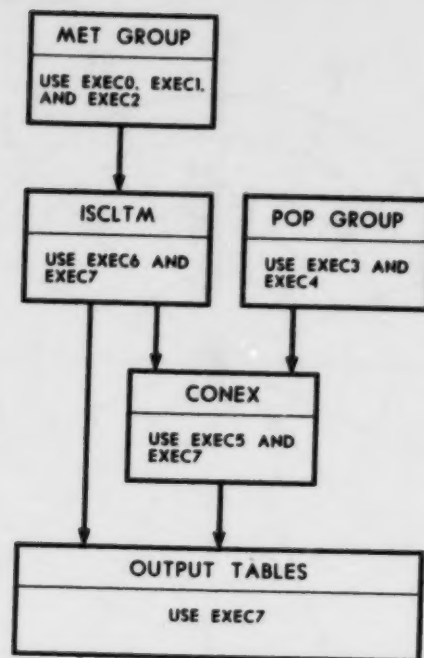


Figure 1. Schematic representation of program group interactions in IEM.

characterized by a set of radial distances to rings circumscribed about the origin and a common set of angles representing sixteen direction vectors. The coordinate systems have a common origin. The relative orientation of the coordinate systems, as built into IEM, is shown in Fig. 2.

The "grid" system is represented by the solid rings in Fig. 2. Intersections of the rings and the direction vectors (D1-D16) mark the points at which ISCLTM calculates ground-level air concentrations (e.g., points G1 and G2). The "centroid" system is represented by the broken rings. Intersections of these rings and the direction vectors (e.g., point C1) locate the centers of sector segments (represented by the hatched area). The POP program group assigns an appropriate number of persons to each sector segment and the CONEX program calculates an average

air concentration over each sector segment using the adjacent "grid" concentrations. CONEX then combines the population and average concentration values to calculate exposures in each sector segment.

PROGRAM GROUPS

The MET (Meteorological Data) Group

The MET group consists of three sequentially executed computer programs, each controlled by its own EXEC routine. These routines provide step-by-step guidance for preparing a region-specific meteorological data set for use by ISCLTM.

The first program, SERCH (controlled by EXEC0), locates and identifies meteorological weather stations near the site being considered. Stations may be located by state or

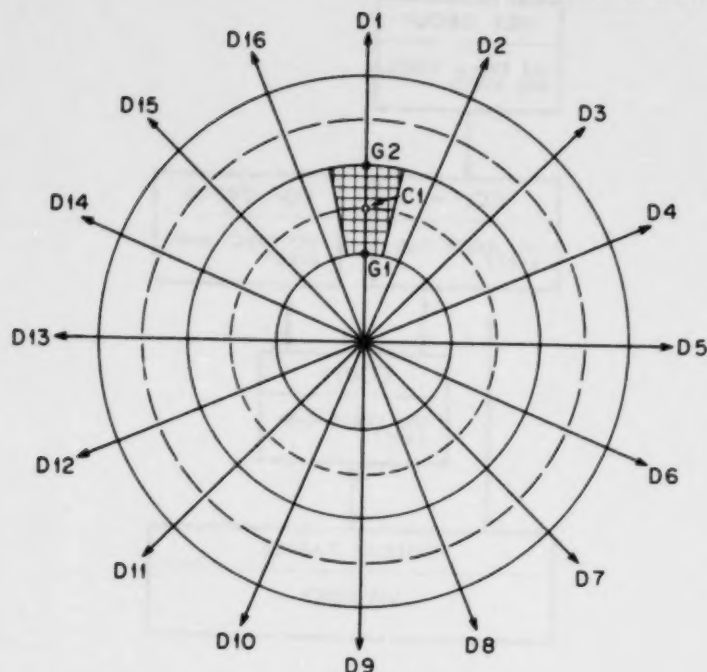


Figure 2. The coordinate systems used in IEM.

latitude-longitude window. Output from SERCH consists of the five-digit station number, name and location (city, state, and latitude and longitude), and the Federal Information Processing Standards (FIPS) state code of each station located in the search area. The number of stations located in the area is also indicated. The user notes the station numbers of all potentially useful weather stations.

Using the noted station numbers, the second program, DIREC (controlled by EXEC1), supplies a description of the available STAR data sets for each potentially useful weather station. In addition to the information supplied by SERCH, DIREC lists for each data set its header number, tape location information (i.e., starting

record number, number of records, and tape number), and a description of the data contained (e.g., time period covered, seasons or months included, etc.). From this information, the user selects a data set for use by ISCLTM.

The user then supplies the information provided by DIREC for the selected data set to the next program, STAR (controlled by EXEC2), which formats the selected data set for use by ISCLTM. This reformatted data set is stored in a semi-permanent data file.

The POP (Population Data) Group

The POP group consists of two sequentially executed computer programs, each controlled by its own

EXEC routine. These routines provide step-by-step instructions for transforming 1980 census population data into a site-specific population distribution for use by CONEX.

The first program, RD80 (controlled by EXEC3), reads grid-recorded 1980 census population data for the region surrounding the site and transforms it into a format suitable for use by the second program. Two types of data sets are available as permanently stored files. A coarse-grid data set contains estimates of the number of persons residing in each cell of a 6'-latitude x 6'-longitude rectangular matrix. (At 36 degrees latitude, each cell is approximately an 11.01 x 9.01 km rectangle.) A fine-grid data set contains similar estimates for each cell of a 2'-latitude x 2'-longitude rectangular matrix. Fine-grid data sets are available for 54 high-population areas (see Table 3.1 of O'Donnell et. al., 1983). To run EXEC3, the user must supply the latitude and longitude of the site (the origin of the coordinate systems), the radial distance to the outermost "grid" ring, and, if applicable, the code name of the fine-grid data set (listed in the users' guide). Output from RD80 is stored as a semi-permanent data file.

The second program, APORT (controlled by EXEC4), is an adaptation of a computer code written by Fields and Little (1978). After the user supplies, through EXEC4, the number of "grid" rings, the distance to each ring, and the latitude and longitude of the origin, APORT uses the data file created by RD80 to produce the population data file needed as input for CONEX. This semi-permanently stored data file contains the number of persons located in each sector segment of the "centroid" system.

The Atmospheric Dispersion Program (ISCLTM)

The atmospheric dispersion program, ISCLTM, is a slightly modified version of the Industrial Source Complex Dispersion Model - Long Term (ISCLT, Bowers et al., 1979). This program calculates the average ground-level air-concentration of a pollutant at each "grid" point around the chosen site (one or more sources) which emits the pollutant. Input to ISCLTM is supplied by the semi-permanent meteorological data file produced by the MET group and an interactively created data file that is prepared using EXEC6. The program is run using EXEC7, which also controls program outputs.

ISCLTM and ISCLT are essentially identical. All modifications to ISCLT were necessitated by the addition of two control switches; they do not affect the calculations performed by the program. One switch directs the program to obtain meteorological data from the data file created by STAR. The second switch creates a temporary output file for use by CONEX.

ISCLT is a steady-state Gaussian plume model and is one of the EPA's recommended air quality models. It can account for settling and dry deposition of particles, downwash, and plume rise as a function of downwind distance. It can be used to simulate the dispersion of nonreactive gases or reactive gases that decay exponentially. ISCLT has the capability to model numerous point, area, and volume emission sources within a facility simultaneously. This model is applicable for sites having flat to gently rolling terrain; receptor elevations may be no

higher than the height of the shortest stack source at the site. Terrain elevation is ignored for area and volume sources.

EXEC6 directs the user in preparation of a permanently stored input data file for use by ISCLTM. (See Bowers et al., 1979 for a detailed explanation of input requirements.) To coordinate ISCLTM with the other IEM programs and to reduce the quantity of interactively input data, many of the input variables have been assigned preselected values (see Table 4.1 of the IEM users' guide). Most preevaluated variables pertain to the control switches and meteorological data descriptors. Source, site, and pollutant variables must be entered by the user.

Outputs from ISCLTM include the standard ISCLT line printer output and the temporary file used by CONEX. The line printer output lists the input data and gives tables of ground-level air concentrations for each source individually and for all sources combined. The temporary file contains the "grid" system coordinates and the source-specific concentration arrays.

The Concentration-Exposure Program (CONEX)

CONEX performs several functions. It (1) rewrites the source-specific concentration estimates from ISCLTM into a variety of tables, including tables of concentrations for selectable source combinations; (2) converts concentrations at "grid" points (from ISCLTM) into average concentrations over the sector segments defined by the "centroid" coordinates; (3) prepares tables of sector segment concentrations; (4) multiplies the sector segment concentrations by the number of persons in

corresponding sector segments (from APORT) to produce sector-segment exposures; (5) prepares tables of the sector-segment exposures; and (6) calculates and tabulates various combinations of the sector-segment exposures. Input data is supplied to CONEX from ISCLTM, APORT, and a user prepared input data file that is created interactively using EXEC5. Program execution and output are controlled by EXEC7.

EXEC5 asks the user to select the desired output tables and to enter values for 14 variables that describe the coordinate systems and give the source and pollutant names and emission rates (see O'Donnell et al., 1983). Some of these variables must be coordinated with those used in ISCLTM and APORT. Available output tables include a matrix of the number of persons assigned to each sector segment; three sets of five tables, one set describing pollutant concentrations at the "grid" points, one describing average pollutant concentrations over each sector segment, and one describing exposures in each sector segment; and four tables that summarize exposures by source, by sector and source, by radial band and source, and by concentration level and source.

FACTORS AFFECTING IEM EXPOSURE ESTIMATES

Factors affecting IEM exposure estimates include the calculated grid-point and segment-averaged ground-level air concentrations, the total number of exposed persons, and the assignment of air concentrations to exposed persons. Since grid-point concentrations are produced by ISCLT, which is documented elsewhere (Bowers et al., 1979 and Bowers and Anderson, 1981), this aspect of IEM is not discussed here. The remaining factors

which interact strongly are discussed briefly below.

In IEM, a segment-averaged air concentration is calculated by taking the logarithmic average of the concentrations at two grid points defined by the intersections of the direction vector passing through the center of the segment and the two "grid" rings that bound the segment. For example, the average concentration for the segment shown in Fig. 2 is obtained from the grid point concentrations G1 and G2. It is assumed that all persons assigned to a segment are exposed to the average concentration estimated for that segment.

Persons are assigned to segments as follows. A coarse- or fine-celled rectangular matrix is superimposed over the area of interest - the area bounded by the closest and farthest grid ring. Some of the cells extend beyond the area of interest. Census (1980) enumeration district populations have been assigned to each cell of the matrix. The number of persons in a cell was taken to be the total number of persons in all enumeration districts that lie within the cell. This total number of persons was assumed to be uniformly distributed over the cell area. The segments of interest are then superimposed over the cells and persons are assigned to a segment in proportion to the fraction of each cell area that lies in the segment. The resulting segment population is assumed to be distributed uniformly over the entire segment area.

Population exposures within each segment are estimated by multiplying the number of persons in the segment by the average air concentration in the segment. The total population exposure is the sum of the segment exposures.

There are other methods of locating exposed persons and assigning air concentrations which can give different results. To determine the significance of such differences, a comparison was made between total human exposure estimates obtained using IEM and estimates obtained using the Human Exposure Model (HEM), which uses a simple atmospheric dispersion algorithm and a different method than IEM of assigning populations to air concentration estimates (Anderson et al., 1980). EPA's Office of Air Quality Planning and Standards (OAQPS) has used HEM for screening-level assessments similar to those performed with IEM. An additional comparison was performed to determine differences due to an alternate, more detailed, complex method of assigning population estimates to each segment (Durfee and Coleman, in press). Durfee's estimates have been used by the Nuclear Regulatory Commission in licensing activities.

To isolate the effect of obtaining and matching population and exposure estimates in each methodology, OAQPS supplied total population exposures around six maleic anhydride plants, which were calculated using the population portion of HEM only. (ISCLT was used to calculate pollutant concentrations.) Results obtained using HEM at the six sites are shown in the right hand column of Table 1. In the left hand column are the total exposures using the IEM coarse population grid, while in the second column are total exposures obtained using the IEM fine grid, when one was available for the site.

Defining "Base" estimates as those made using fine-grid data when available, or coarse-grid data otherwise, IEM estimates can be compared with those obtained using HEM. It can be seen from the bottom half of

TABLE 1. TOTAL EXPOSURE ESTIMATES AT SIX SITES USING IEM
WITH APORT (COARSE AND FINE) AND DURFEE POPULATION
DATA AND HEM WITH EXTRAPOLATED 1970 DATA

Site	IEM (coarse)	IEM (fine)	IEM (Durfee)	HEM
Total exposure (person-ug/m ³)				
West Virginia	25,700	a	29,000	33,600
Missouri	42,900	46,100	50,400	47,300
Indiana	79,500	a	77,500	50,900
Illinois	28,600	a	32,400	38,700
New Jersey	12,000	12,500	11,000	9,540
Pennsylvania	251,000	270,000	287,000	267,000
Total exposure (percent difference from Base) ^b				
West Virginia	Base		12.8	30.7
Missouri	-6.9	Base	9.3	2.6
Indiana	Base		-2.5	-36.0
Illinois	Base		13.3	35.3
New Jersey	-4.0	Base	-12.0	-23.7
Pennsylvania	-7.0	Base	6.3	-1.1

^a No data.

^b Base = IEM fine if available, IEM coarse otherwise.

Table 1 that the total exposures calculated using HEM differ by between -36 and +35 % from those using IEM.

These differences may arise for two reasons. First, the HEM population was an extrapolation of 1970 data to 1980; IEM uses 1980 census population data. As can be seen in Table 2, the total exposed populations estimated by HEM differed by between -13 and +7% from the "base" IEM population estimates. Second, HEM uses a different approach to determining population exposures. It assumes that all persons in a census enumeration district are located at one point and calculates the average concentration at that point by extrapolation, using the concentrations at the four nearest

grid points surrounding the population point.

A comparison of total exposures obtained using Durfee's data is shown in column three of Table 1. In this case differences in the estimates are between +13%. Differences between the three sets of IEM exposure estimates must be due to differences in the population estimates produced by APORT (coarse and fine grid) and by Durfee. This is verified in Table 2, which shows percentage differences (-12 to +9%) in total numbers of exposed persons that generally agree with the percentage differences in total exposures given in Table 1. The lack of complete agreement is explained by the way the three population estimation techniques allocate

TABLE 2. TOTAL POPULATIONS WITHIN 20 km OF SIX SITES AS ESTIMATED BY APORT (COARSE AND FINE), DURFEE, AND HEM

Site	APORT (coarse)	APORT (fine)	APORT (Durfee)	HEM
Total number of persons (thousands)				
West Virginia	56	a	61	52
Missouri	1,242	1,248	1,284	1,338
Indiana	110	a	110	108
Illinois	154	a	164	160
New Jersey	1,424	1,470	1,300	1,277
Pennsylvania	977	1,063	1,094	1,090
Total number of persons (percent difference from Base) ^b				
West Virginia	Base		8.6	-7.3
Missouri	-0.5	Base	2.8	7.2
Indiana	Base		-0.5	-2.1
Illinois	Base		6.7	4.1
New Jersey	-3.1	Base	-11.6	-13.1
Pennsylvania	-8.1	Base	2.9	2.6

^a No data.

^b Base = IEM fine if available, IEM coarse otherwise.

their total populations among the various segments used in IEM.

SUMMARY

These comparisons indicate that the choice of distributing population and computing exposure throughout an impacted area is unlikely to introduce differences in the resulting exposure estimate of greater than $\pm 50\%$. They also show that although there is no discernible bias introduced by the APORT, HEM, and Durfee methodologies over a large range (56,000 to 1,400,000) of population estimates, use of fine-grid data by IEM produces slightly higher (up to 8%) population and exposure estimates than those produced by coarse-grid application alone.

A brief outline of the operation, capabilities, and input data requirements of IEM is given. Important factors affecting IEM exposure estimates are discussed. A six site comparison shows that total exposed population estimates obtained by two other methods differ from IEM estimates by only -13 to +9%. Corresponding exposure estimates show differences between -36 and +35%.

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OPERATION AND MAINTENANCE COST RELATIONSHIPS FOR HAZARDOUS WASTE INCINERATION

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ABSTRACT

This paper outlines the results of an IRB-sponsored study to develop relationships between operation and maintenance (O&M) costs for hazardous waste incineration facilities and the various waste-specific, design-specific, and operational factors that affect these costs. An overview of the cost estimating methodology is presented, followed by a derivation of annual O&M costs for a hypothetical incineration facility.

BACKGROUND

EPA is currently performing a Regulatory Impact Analysis (RIA) of the RCRA performance standards for hazardous waste incinerators. One of the key elements of this RIA effort is development of representative cost data for hazardous waste incineration, including:

- Capital costs for new facilities designed in accordance with RCRA requirements,
- Retrofit costs for existing facilities to comply with the RCRA standards, and,
- Operation and maintenance (O&M) costs for new or existing facilities.

This cost information is also needed by IRB to complement technical/environmental evaluations of hazardous waste incineration technologies, and to aid in identifying future research priorities.

This paper focuses on the IRB-sponsored study of O&M costs for hazardous waste incineration facilities.

OBJECTIVES

The primary objective of the study was to develop relationships between O&M costs for hazardous waste incineration and the various waste-specific, design specific, and operational factors that affect these costs. These cost relationships were to be designed so that annual and unit (\$/lb, etc.) O&M cost estimates could be calculated for a variety of waste compositions, different incineration system operating conditions, and performance requirements. This degree of parametric cost estimation capability was considered essential for the RIA effort and for future IRB utilization.

The second objective of the study was to derive and arrange these cost relationships in computer-ready format, so that they could be easily programmed for cost sensitivity analyses purposes.

OVERVIEW

Based on these objectives, an O&M cost estimation model has been developed in computer-ready, or "workbook" format. Sequential elements of the model are as follows:

- (1) Input data specifications
- (2) Design assumption and engineering calculations
- (3) Variable operating cost calculations
- (4) Semi-variable O&M cost calculations
- (5) Fixed cost calculations
- (6) Energy recovery credit calculations (optional)
- (7) Net, unit O&M cost calculation

Input requirements for the model include basic physical chemical properties of the waste(s) in question plus a limited number of incineration facility design and operating specifications. From these input data and numerous technical assumptions in-line with industry practice and standard material/energy balance relationships, a wide array of engineering calculations are performed to estimate the rates at which fuel, power, and other chemicals/utilities are consumed. These calculated utility/chemical consumption rates are then multiplied by the projected annual utilization percentage for the facility, and then by unit costs for fuel, power, etc., to estimate annual totals for each variable cost element. Energy recovery credits are estimated in the same manner,

although these credits are usually incorporated after the semi-variable O&M costs and fixed charges to capital are estimated.

Both maintenance costs and fixed charges to capital--depreciation, insurance, and taxes--are estimated as percentages of the depreciable fixed capital investment (DFCI) for a given incineration facility. As discussed under continuing research at the end of this paper, capital cost estimating procedures are currently being developed to complement this O&M cost estimation model and provide DFCI input values for maintenance and fixed cost estimation.

The final step in the O&M cost estimating procedure is the unit disposal cost calculation. This is accomplished by summing the annual variable costs, semi-variable costs, fixed charges to capital, and energy recovery credit, prior to division by the total quantity(s) of waste(s) incinerated annually.

INPUT DATA SPECIFICATIONS

For input data specification purposes, wastes are divided into five categories; combustible organic liquids, noncombustible liquids (without support fuel), pumpable slurries or sludges, non-pumpable sludges or bulk solids, and containerized solids.

The following data are requested for each waste stream, all of which must be relegated to one of the

above categories:

- Feed rate, average lb/hr
- Heating value, typical Btu/lb
- Fractional content of carbon, hydrogen, oxygen, nitrogen, moisture, ash, and chlorine (as received)
- Whether or not alkali metals or toxic, heavy metals are present in the ash

Certain facility design and operating conditions must also be specified to use the model, including:

- Owner/operator designation
- Generic incinerator design-liquid injection, rotary kiln, or multiple chamber, hearth type
- Incinerator capacity, Btu/hr plus liquid and solid feed rate limitations
- Incinerator exit gas temperature (secondary chamber temperature for kiln and hearth incinerators)
- Whether or not a waste heat boiler is utilized for energy recovery
- Particulate emission limitations, gr/dscf
- HCl emission control requirements, overall efficiency
- Operating schedule, hours/day and days/week
- Total annual on-stream time, or percentage utilization

This input data should be self-explanatory with the exception of "owner/operator designation." Three distinct owner/operator scenarios are provided so that the economic impacts of regulation can be evaluated across different segments of the hazardous waste incineration user industry. These three scenarios are summarized in Table 1.

Obviously, certain waste characteristics and design alternatives that can impact costs have been passed over at this point. First of all, wastes containing significant concentrations of sulfur, phosphorus, or halogens other than chlorine are not provided for. This limitation is imposed because (a) few of these type of wastes are listed for RCRA purposes and (b) assessment of air pollution control costs would be beyond the scope of the study if such waste types were to be considered.

In a similar vein, air pollution control device (APCD) selection is limited to venturi scrubbers for particulate control and packed bed absorbers for acid gas (HCl) removal. These limitations are realistic because venturi and packed bed scrubbers are the choice of most designers. However, there is a recent trend toward ionizing wet scrubbers (IWS's) for particulate control in large facilities to eliminate the substantial back pressure associated with venturi scrubber operation.

TABLE 1. OWNER/OPERATOR SCENARIOS

	Scenario A	Scenario B	Scenario C
Owner/Operator	Institution (e.g., University plant or refinery)	Industrial Plant (e.g., chemical plant or refinery)	Commercial waste disposer (corporate central or semi- private facility)
Source of waste	100 percent onsite	100 percent onsite	100 percent offsite
Liquid injection and rotary kiln incinerator capacities	1 to 10 million Btu/hr	10 to 50 million Btu/hr	50 to 100 million Btu/hr
Hearth incinerator capacities	1 to 10 million Btu/hr	10 to 50 million Btu/hr	--
Liquid waste delivery method	Small containers, multiple onsite sources	Pumping from process(es)	Tank trucks from offsite (plus some drummed liquids)
Liquid waste storage practices	Bulk storage, single tank per waste type, minimal segregation (high Btu/low Btu)	Bulk storage, dual tanks per waste type, minimal segregation (high Btu/low Btu)	Bulk storage, dual tanks per waste type, extensive segregation for blend optimiza- tion
Liquid waste blending (other than storage)	No	No	Yes
Solid waste form as delivered, stored, and fired	Bulk or very small (5-gal) containers containers	Bulk or small (≤ 30 gal) containers	Bulk, small con- tainers or 55-gal drums
Solid waste feed method	Semiautomatic	Semiautomatic	Automatic for bulk solids, semiauto- matic for drums
Bottom ash removal method	Manual	Automatic	Automatic
Energy recovery	No	Optional	Optional, but improbable
Quench/scrubber water source	Municipal supply	Onsite WWTP effluent, private well, or municipal supply	Local WWTP effluent, private well, or municipal supply
Scrubber blowdown	Municipal sewer	Onsite WWTP (central facility)	Onsite WWTP (specialized or central) or municipal sewer
Administrative/ clerical labor required	No	No	Yes
Frequent waste analyses required	No	No	Yes
Standard operating schedule	8 hr/day, 5 days/week	24 hr/day, 7 days/week	24 hr/day, 7 days/week

Some large facilities also use tray tower scrubbers rather than packed beds for acid gas removal; however, the differences in operating costs are less pronounced in this case.

DESIGN ASSUMPTIONS AND ENGINEERING CALCULATIONS

Before the input data listed above can be used to estimate O&M costs, a number of design assumptions and engineering calculations are needed to estimate raw material and utility consumption rates. The design assumptions incorporated in the model are too numerous to address in this forum in their entirety; however, the major overlying assumptions are as follows:

- (1) Either liquid injection, rotary kiln, or multiple chamber hearth incinerators are used. Unique, exotic, or hybrid designs are not considered.
- (2) Incinerators are equipped with sufficient No. 2 fuel oil firing capacity to reach the designated operating temperature prior to waste injection.
- (3) Bottom ash from kiln and hearth incinerators is disposed off-site at sanitary or secure landfills, depending on ash component toxicities.
- (4) Firetube and watertube waste heat boilers are the only energy recovery devices considered. Where utilized, waste heat boilers are located immediately downstream from the incinerators, reducing combustion

gas temperatures to 550°F.

- (5) Waste heat boilers are followed by small in-line quenches to reduce gas temperatures to 200°F upstream from scrubbing devices. If waste heat boilers are not employed, larger quenches are used to achieve the same temperature reduction. Quench feedwater is fresh, rather than recycled, to limit entrainment of dissolved solids as submicron particulate.
- (6) Three air pollution control system configurations are considered:
 - a) Venturi scrubber for particulate control
 - b) Packed bed absorber for HCl removal
 - c) Venturi scrubber followed by packed bed absorber for combined particulate and HCl control.

It is assumed that at least one air pollution control device is needed for all hazardous waste incineration systems. Otherwise, the waste would be a fuel-quality material suitable for more profit-able end use.

- (7) All scrubbing systems have a common sump which receives the quench, venturi scrubber, and absorber effluents. At least 5% of the combined effluent is discharged to limit solids buildup, with the remainder recycled to the scrubbers.
- (8) Caustic soda solution is used in stoichiometric quantities for HCl scrubbing.

- (9) All systems are assumed to be balanced draft, with combustion air blowers for the incinerators and ID fans downstream from the scrubbing devices.
- (10) Facility operators are reasonably competent in controlling costs. For example, no auxiliary fuel is burned if the waste will sustain combustion with a reasonable excess air allowance at the designated incinerator temperature.
- (11) The overall system is adequately designed in terms of safety interlocks and materials of construction to prevent catastrophic failure.

These design assumptions are typical of good practice in the hazardous waste incineration user industry. Therefore, they provide a realistic basis for O&M cost estimation for the industry as a whole, which is the goal of the RIA. However, these assumptions do not reflect current practice for all facilities, so O&M cost estimates derived from the model may not be representative for specific facilities. This point is discussed further at the conclusion of the paper.

Based on these design assumptions and the input data previously described, numerous engineering calculations are performed to determine raw material and utility consumption rates. For the most part, these are standard material and energy balance calculations as summarized below.

- Front-end storage and handling equipment operation
 - Tank agitator power requirements
 - Liquid nitrogen requirements for tank blanketing
 - Steam requirements for tank heating
 - Liquid waste transfer and feed pump power requirements
 - Fuel consumption by solid waste transfer vehicles
 - Solid waste conveyor/feeder power requirements
 - Atomizing air compressor power requirements
- Incinerator operation
 - Waste component feed rates and gross heat input
 - Low-fire fuel consumption for flame stabilization
 - Supplemental fuel and total air feed requirements
 - Fuel oil feed pump power requirements
 - Combustion air blower power requirements
 - Combustion gas flow and composition
 - Particulate loading in combustion gases
 - Charge stoking and bottom ash handling requirements for solid waste incinerators
 - Start up fuel requirements
- Waste heat boiler operation
 - Steam generation rate
 - Fuel conservation rate
- Quench operation
 - Heat duty and water requirements
 - Feed pump power requirements
- Scrubber system operation
 - Venturi scrubber pressure drop requirements
 - Venturi scrubbant feedrate requirements
 - Venturi scrubbant recycle pump power requirements
 - Venturi scrubber effluent and exit gas flowrates

- Blowdown rates and scrubber system makeup water requirements
- Makeup water pump power requirements
- ID fan power requirements

VARIABLE OPERATING COST CALCULATIONS

The variable operating cost elements addressed in the model are as follows:

- (1) Fuel
 - Natural gas for flame stabilization
 - No. 2 fuel oil for supplemental heat input
 - No. 2 fuel oil for startup
 - Propane for lift truck operation
- (2) Power
 - Liquid waste/fuel oil feed pumps
 - Quench/scrubber system pumps
 - Solid waste conveyors and feeders
 - Solid waste incinerator mechanical requirements (e.g., kiln rotational drive)
 - Combustion air blower(s)
 - Atomizing air compressor
 - ID fan(s)
 - Tank agitation
- (3) Water
 - Quench/scrubber system makeup
 - Ash quenching
- (4) Caustic soda solution (50 wt%) for acid gas scrubbing
- (5) Liquid nitrogen for tank blanketing

- (6) Steam for tank heating (expressed as additional fuel cost for the main plant boiler complex)
- (7) Ash and scrubber blowdown disposition

Annual costs for these utilities and supplies are determined from the results of the preceding engineering calculations (which predict hourly consumption rates), the projected annual utilization percentage for the facility, and unit costs for fuel oil, electric power, etc. In the first generation model, Houston area costs alone were included. Since then, an option has been designed in so that East Coast (New Jersey), Midwest (Chicago), or West Coast (Los Angeles) costs can be used in place of the Houston, Gulf Coast costs.

SEMI-VARIABLE O&M COSTS

The semi-variable O&M cost elements include:

- (1) Operating labor and supervision
- (2) Maintenance materials and labor
- (3) Incoming waste analyses

Unlike the variable cost elements such as power and water, these costs cannot be annualized as a function of the total facility on-stream time. Labor costs are relatively consistent throughout the 12-month period, depending more on (a) the hours/day, days/week operating schedule, (b) whether or not solid wastes as well as liquid wastes are handled, (c) the degree of automation employed, and (d) how closely the incineration operation is tied to the waste

generating operations, if at all. The model presents six scenarios for heuristic labor cost estimation, taking each of these factors into account. These scenarios are summarized in Tables 2-4.

For most hazardous waste incineration facilities, maintenance costs are the most difficult to predict apriori. These costs are influenced by so many detailed waste-vs-equipment design considerations that parametric evaluation is almost impossible. Moreover, the major maintenance requirements such as refractory replacement are affected by subjective criteria such as adequacy of the original design and operator experience. Therefore, the simple approach is used for maintenance cost estimation based on percentage of the depreciable fixed capital investment. The multipliers are 5% for liquid injection systems, 7% for multiple chamber hearth systems, and 10% for rotary kiln systems.

Annual costs for analysis of incoming wastes are wholly dependent on the nature of the waste generating operation(s). These costs may run from essentially zero to the burdened labor cost for one technician, 40 hours/week.

FIXED COST CALCULATIONS

Depreciation, insurance, and taxes are all estimated as percentages of the depreciable fixed capital investment for the facility. Ten-year, straight line depreciation is assumed with essentially zero salvage value, while insurance and taxes are assumed to total 4% of the depreciable fixed capital investment.

ENERGY RECOVERY CREDIT CALCULATION

For the purposes of this model, the only energy recovery option considered is steam generation in a waste heat boiler. The value of the steam generated is calculated in terms of potential fuel savings for the plant-wide boiler complex, assuming equivalent steam enthalpies as-delivered, 80% fuel-to-steam efficiency in the boiler complex, and that No. 2 fuel oil is utilized.

UNIT DISPOSAL COST CALCULATION

The unit cost for waste disposal by incineration is easily calculated at this point by the relationship:

$$\begin{aligned} & (\text{Annual Variable Cost}) + \\ & (\text{Annual Semi-Variable Cost}) + \\ & (\text{Annual Fixed Cost}) - \\ & (\text{Annual Energy Recovery Credit}) \end{aligned}$$

(Annual Quantity of Waste Incinerated)

This is the bottom-line figure for comparing one incineration O&M cost estimate to another.

EXAMPLE

In order to illustrate the inputs and outputs of the model, the following, simplified example is provided.

Input Data Specifications

Waste description: Mixture of contaminated solvents and process byproducts.
Normal feedrate : 2000 lb/hr
Heating value: 8000 Btu/lb

TABLE 2. ESTIMATED LABOR REQUIREMENTS FOR CATEGORY A FACILITIES

Labor category	Liquid wastes only			Liquid and solid wastes		
	Number per shift	Number of shifts	Total number of personnel	Number per shift	Number of shifts	Total number of personnel
Process operator	1	1	1	1	1	1
Forklift operator	0	0	0	1	1	1
Yard laborer	0	0	0	1	1	1
Engineering supervisor	0.25	1	0.25	0.25	1	0.25

TABLE 3. ESTIMATED LABOR REQUIREMENTS FOR CATEGORY B FACILITIES

Labor category	Liquid wastes only			Liquid and solid wastes		
	Number per shift	Number of shifts	Total number of personnel	Number per shift	Number of shifts	Total number of personnel
Process operator	1	4	4	1	4	4
Forklift operator	0	0	0	1	4	4
Yard laborer	0	0	0	1	4	4
Engineering supervisor	0.5	1	0.5	0.5	1	0.5

TABLE 4. ESTIMATED LABOR REQUIREMENTS FOR CATEGORY C FACILITIES

Labor category	Liquid wastes only			Liquid and Solid wastes		
	Number per shift	Number of shifts	Total number of personnel	Number per shift	Number of shifts	Total number of personnel
Process Operator	3	1	--	3	1	--
Forklift Operator	2	3	9	2	3	9
	0	0	0	1	4	4
Yard laborer	0	0	0	1	4	4
Clerical	0.5	1	0.5	0.5	1	0.5
Engineering Supervisor	1	1	1	1	1	1
Administrator	1	1	1	1	1	1

Composition: Carbon 54.5%
 Hydrogen 3.5%
 Chlorine 5.0%
 Moisture 19.5%
 Ash 0.5%
 Oxygen 9.0%
 Nitrogen 8.0%

Owner/operator designation:
 B (chemical plant)
 Generic incinerator design
 type: Liquid injection
 Total thermal capacity:
 20M Btu/hr
 Operating temperature:
 2000°F
 Energy recovery utilization:
 No
 Maximum particulate loading:
 0.08 gr/dscf
 HCl removal efficiency: 99%
 Operating schedule: 24 hr/day,
 7 day/week
 Annual utilization: 80%
 Location: Houston, Texas
 Estimated depreciable fixed
 capital investment: \$1.5M

Raw Material/Utility Consumption Rates

Based on the input data listed above, estimated raw material and utility consumption rates for the hypothetical facility are summarized in Table 5.

O&M Costs

Annual O&M costs and credits for the hypothetical facility are summarized in Table 6. The unit costs are in mid-1982/early 1983 dollars and are representative of the Houston area.

Unit Disposal Cost

The unit disposal cost is given by the expression,

Unit disposal cost, \$/lb.=

Net, annual O&M cost, \$
 Total annual waste throughput, lb.

For this hypothetical case, the unit disposal cost is approxi-

mately \$0.053/lb.

CONCLUSIONS

The O&M cost estimation model for hazardous waste incineration described and illustrated in the preceding pages should be accurate to within ± 30 -40% for all but the most unusual cases. This is consistent with normal conceptual design goals for cost estimating accuracy, and should be suitable for purposes of the RIA as well as for EPA research planning purposes. This model should also be useful to waste generators making first-cut cost comparisons between on-site incineration and other, off-site disposal options. However, the model is limited in its ability to accurately predict site-specific costs, so it is not recommended for cost estimating purposes beyond the conceptual design stage.

CONTINUING RESEARCH

In FY 1983, the existing O&M cost model will be expanded and augmented in the following manner:

- (1) A corollary capital cost estimation model for hazardous waste incineration will be finalized.
- (2) The air pollution control system options will be expanded to include IWS-based systems as well as the more standard venturi scrubber/packed bed absorber system.
- (3) Capital and annual cost/credit estimation models will be developed for other thermal destruction

TABLE 5. ESTIMATED RAW MATERIAL/UTILITY REQUIREMENTS

<u>Item</u>	<u>Normal Rate</u>	<u>Total annual quantity</u>
Fuel		
Natural gas for flame stabilization	1000 scfh	7M ft ³
No. 2 fuel oil for startup	110 gal/startup	1400 gal
Power		
ID fan	95 hp	-
Compressor	70 hp	-
Blower	35 hp	-
Pumps	20 hp	-
Agitators	nil	-
Total	220 hp	1.15 Gwh
Water	110 gpm	48 M gal
Caustic soda solution (50 wt %)	230 lb/hr	1.6 M lb
Liquid nitrogen	38 ft ³ /hr	270 M ft ³
Sewer use	110 gpm	45 M gal

TABLE 6. ESTIMATED ANNUAL O&M COSTS AND CREDITS

<u>Item</u>	<u>Unit Cost</u>	<u>Annual Cost</u>
Natural gas	\$5.00/1000 ft ³	\$35,000
No. 2 fuel oil	0.85/gal	1,200
Power	0.061/kwh	70,000
Water	0.25/1000 gal	12,000
Caustic soda solution (50 wt %)	0.07/lb	110,000
Liquid nitrogen	1.06/100 ft ³ (+\$2,400/yr tank rental)	5,200
Sewer	1.29/1000 gal	58,000
Labor	See table 3	160,000
Maintenance	-----	75,000
Depreciation	-----	150,000
Insurance/taxes	-----	60,000
TOTAL		\$736,400

techniques such as boiler and cement kiln co-firing.

Finally, an effort is underway to validate both the existing O&M cost model and the other models now being developed.

RETROFIT COST RELATIONSHIPS FOR EXISTING HAZARDOUS WASTE INCINERATION FACILITIES

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ABSTRACT

This paper outlines the results of an IRB-sponsored study of potential retrofit costs for hazardous waste incineration facilities. Cost relationships are presented for major capital additions or modifications that could be required to bring existing facilities into compliance with RCRA performance regulations. A hypothetical retrofit cost scenario is also presented.

BACKGROUND

EPA is currently performing a Regulatory Impact Analysis (RIA) of the RCRA performance standards for hazardous waste incinerators. One of the key elements of this RIA effort is development of representative cost data for hazardous waste incineration, including:

- Capital costs for new facilities designed in accordance with RCRA requirements,
- Operation and maintenance (O&M) costs for these facilities, and
- Retrofit costs for existing facilities to comply with RCRA standards.

This paper describes the IRB-sponsored study of retrofit costs for hazardous waste incineration facilities

PURPOSE AND SCOPE

The objective of this study was to develop a methodology, and an accompanying set of empirical cost relation-

ships, that could be used to estimate the costs of retrofitting/upgrading various components of existing hazardous waste incineration facilities to comply with RCRA performance requirements. Both the methodology and the retrofit cost relationships were intended to focus on major capital additions or subsystem modifications that could be required for existing facilities to:

- (1) Increase destruction and removal efficiency (DRE) of the principal organic hazardous constituents (POHC's) in the waste feed,
- (2) Reduce particulate loading in the stack gas to <0.08 gr/dscf, and/or
- (3) Increase HCl removal to $>99\%$ in facilities burning a waste mix containing 0.5% organic chlorine.

Because the performance status of many incineration facilities is unknown, particularly with respect to DRE, it was not possible

to predict within the framework of this study what the actual retrofit requirements for various segments of the incinerator population might be in order to comply with RCRA standards. In all likelihood, many existing facilities will require no physical modification to meet these standards. Other facilities may require extensive, multiple component modifications. For still others, retrofit may not be feasible because of space or equipment design limitations. Therefore, this study was not designed to predict what the total retrofit costs would be for the hazardous waste incineration user industry to comply with RCRA requirements. Rather, the results of the study were intended as a cost estimating tool for EPA decision making purposes. The scenario envisioned for application of the methodology and cost relationships developed in his study was, "If one or more capital additions/modifications are required for Facility XYZ to achieve RCRA compliance, and Facility XYZ has the following design/operational characteristics, what will it cost to make the necessary modifications?"

At the onset of the study, it was recognized that major capital additions or modifications were not the only types of retrofit costs that may be encountered by facilities upgrading performance. Others include minor finetuning adjustments, downtime-related costs, and increased O&M costs. However, these costs could not be quantified within the framework of this study.

OVERVIEW OF RESULTS

The results of this study are expressed in a series of empirical (graphical) relationships between the costs for various capital modifications/additions and factors that significantly impact these costs, e.g., capacity, materials of construction, etc. These curves were derived as the result of queries to a number of vendors of incinerator equipment. Costs are developed for:

- Combustion system retrofit
 - Burner replacement
 - Refractory replacement
 - Combustion chamber replacement
- Quench and/or waste heat boiler addition
- Scrubber system addition, replacement, or modification
- Flue gas handling system modification
 - Fans, stack, etc.
- Total system replacement

In addition to the cost curves themselves, guidelines are presented to aid the user in determining when particular retrofit activities need to be considered, what types of input data are needed to use the various cost curves, and how installation, indirect construction costs, and contingencies can be factored in.

The cost relationships and associated information are designed to cover as broad a range of incinerator facility scenarios as possible, although certain cases may

not be addressed. A wide range of possible waste compositions are considered; hydrocarbon-based mixtures with variable heating values, moisture contents, ash contents and compositions (including alkalis), and chlorine concentrations. Liquid injection, rotary kiln, and hearth-type incinerators are all addressed in capacities ranging from 1-100 M Btu/hr. Both quenches and steam-generating waste heat boilers with or without economizers are considered for gas temperature reduction, venturi scrubbers are assumed for particulate control, and packed bed absorbers are assumed for HCl removal. Uncontrolled pollutant concentrations entering the air pollution control system are assumed to range from 0-2 gr/dscf for particulate and <2 vol % for HCl. These ranges are believed to cover the range of conditions experienced in existing hazardous waste incineration facilities.

The following sections describe the cost relationships for various retrofit activities in more detail.

COMBUSTION SYSTEM RETROFIT

The primary driving force considered in this study for combustion system retrofit was to increase destruction efficiencies (DE's) for POHC's contained in the waste. At the present time, insufficient data is available to relate DE's directly to incinerator design and operational requirements. Therefore, this study focused on major capital additions or modifications that might be needed to raise incinerator temperature above

original design specifications and/or to increase effective residence time, mixing efficiency, etc.

The first potentially major cost item considered was burner system replacement for improved combustion efficiency or increased fuel co-firing capability to elevate temperature. The major problem encountered in estimating the costs for this activity was that high-efficiency burners capable of handling multiple liquid waste streams plus support fuel are almost always custom designed and fabricated. Thus, the costs are quite case-specific and difficult for manufacturers to generalize. The alternative adopted for this study was a baseline costing approach whereby a purchased cost vs. capacity curve was developed for burner systems capable of firing waste oils. This curve is shown in Figure 1. Burner auxiliaries such as blowers, dampers, flame safeguards, and combustion controls are included in the costs. Installation is assumed to be 50% of purchased cost. A major underlying assumption is that the burner system is physically compatible with the combustion chamber configuration. If not, more extensive retrofit activities are required as will subsequently be described.

If incinerator temperature is increased substantially above the original design specifications, it may be necessary to replace the existing refractory lining

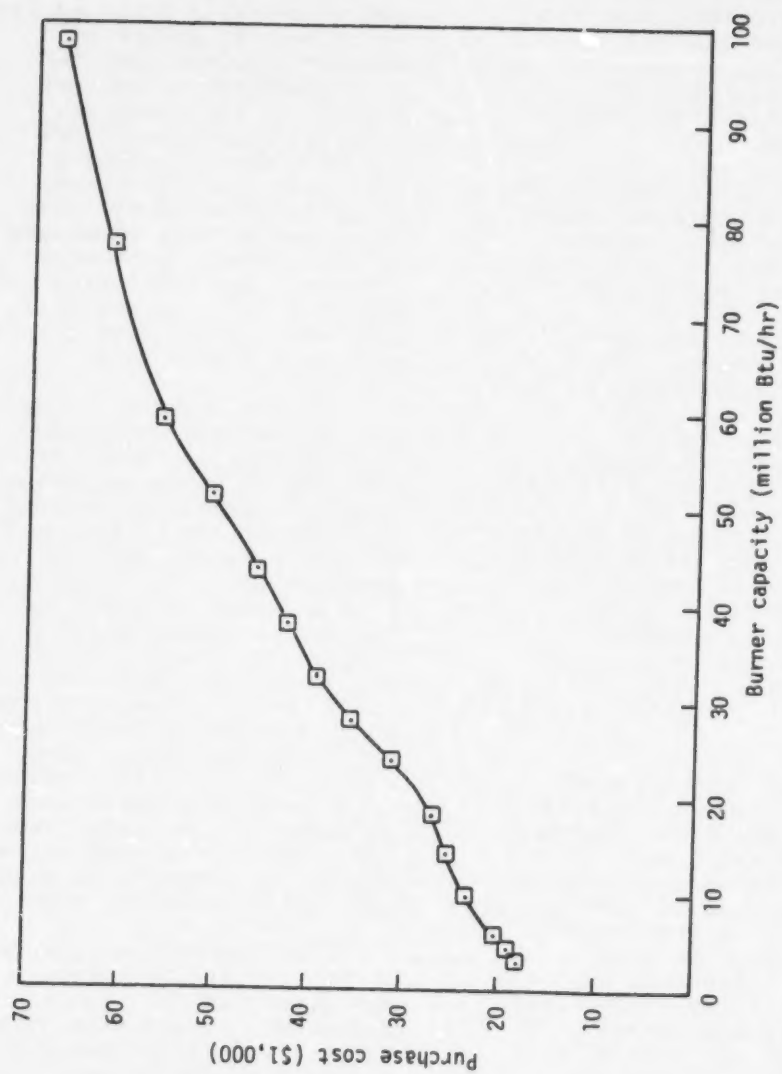


Figure 1 Purchase cost of new burners (July 1982).

with a higher grade material. For the purposes of this study approximate refractory replacement costs are estimated by first calculating the material requirements, then judging the type of refractory required and its cost, and finally, factoring in labor costs for removal of the old lining and installation of the higher quality material.

The volume of refractory required for a given application is estimated, in brick equivalents (9 in. X 4.5 in. X 3 in.) from the thermal capacity of the system, typical state-of-the-art heat release rates and residence times for the three generic incinerator designs considered, typical dimensions for these generic designs (length: diameter, surface: volume), and simplified thickness vs. temperature guidelines. For a typical 30 M Btu/hr liquid waste furnace, the design assumptions would be a 30,000 Btu/hr ft^2 heat release rate, a 3:1 length-to-internal-diameter ratio, a 4.5-6 in. inner lining of firebrick, and a 2.5-3 in. outer lining of insulating refractory.

Refractory "type" (brick vs. castable, alumina content) and unit cost are then estimated based on temperature application guidelines, plus the qualitative presence or absence of alkalis and/or chlorine in the combustion environment. Usually a 45% alumina refractory is satisfactory for low temperature (1400-1800°F) applications. For temperature up to 2400°F and/or corrosive environments, a 60-80% alumina refractory is normally specified. For exotic applications above 2400°F, a 90% alumina content is needed. Costs range from less than \$1 per brick equivalent to

more than \$10 per brick equivalent.

Total material costs are then determined by combining the estimated volume requirements in brick equivalents and the dollar per brick equivalent cost for an appropriate refractory. A range of installed vs. material cost multipliers are provided to estimate the final installed cost, which is affected by local labor costs, ease of access to the combustion chamber interior, and other site specific factors. Installation-to-material-cost ratios can range from 1 to 4.

In many cases, it may not be feasible to replace only the burner system or only the existing refractory; complete combustion system replacement may be required to significantly improve performance. For example, a substantial increase in operating temperature may require a thicker refractory lining to limit skin temperature. This increased refractory thickness reduces internal volume and residence time. If the residence time reduction is significant enough to impact DE, a larger shell and, thus, a new combustion chamber is required to provide sufficient residence time.

In Figures 2-4 equipment cost vs. capacity curves are presented for liquid injection, rotary kiln/afterburner, and fixed hearth/afterburner combustion systems. The costs include burner systems, as previously described, refractory lined shell, auxiliaries, and controls. Feed system costs are not included.

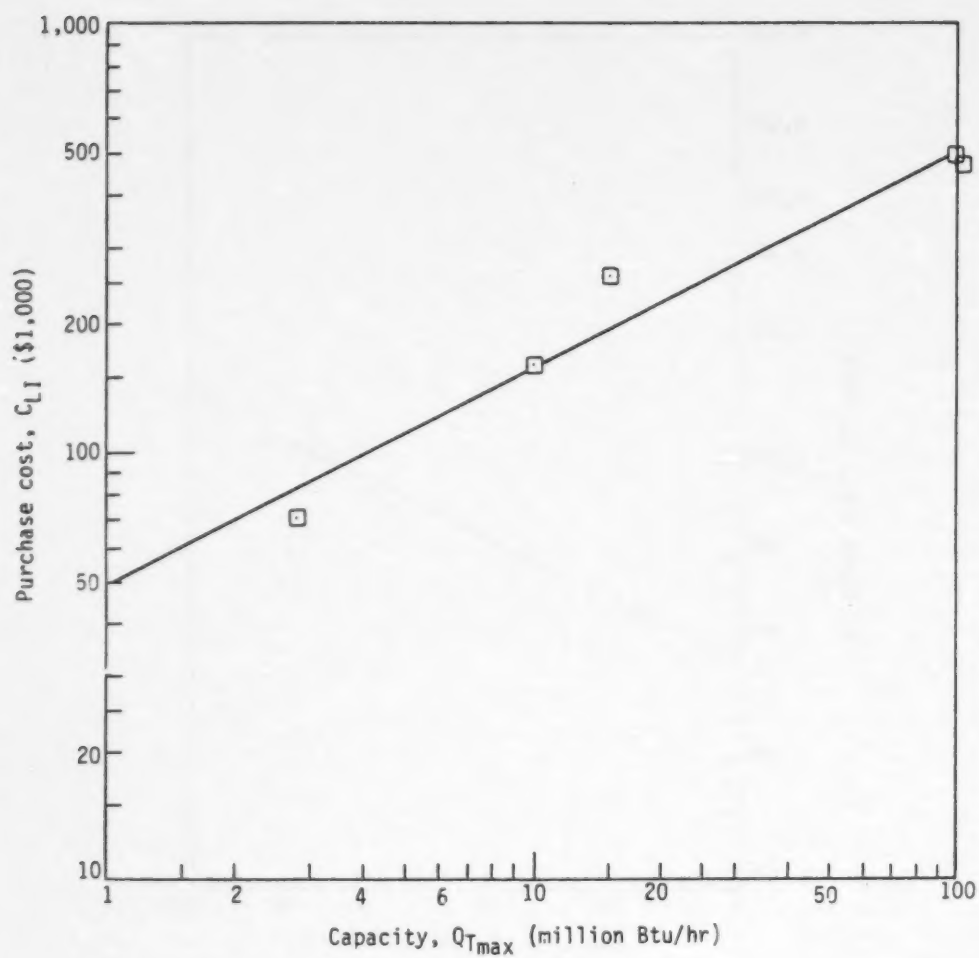


Figure 2. Purchase cost of liquid injection incinerators (July 1982).

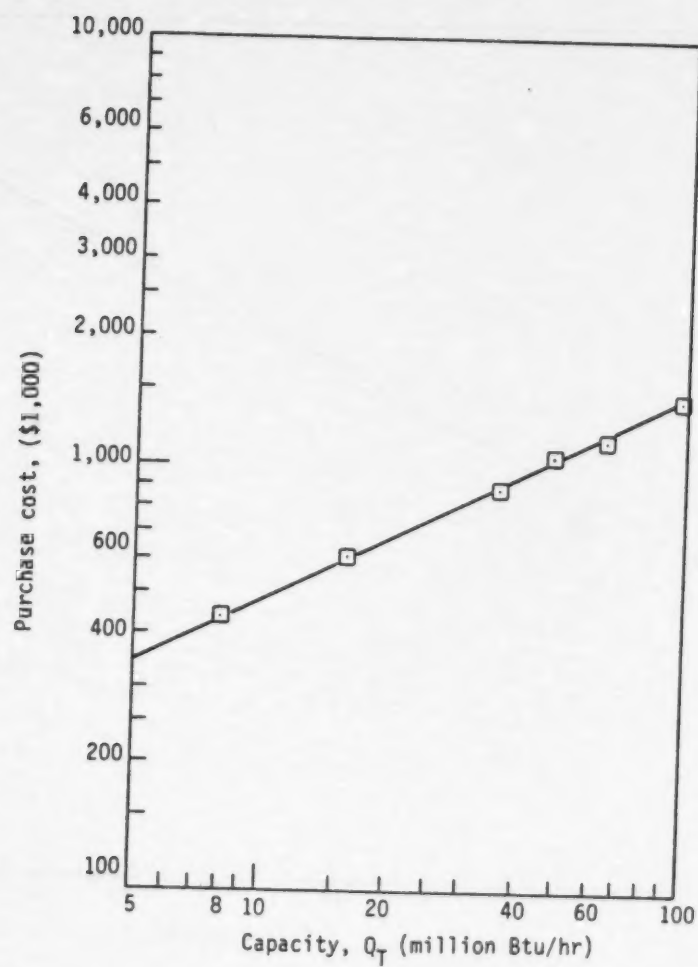


Figure 3. Purchase cost of rotary kiln incinerators (May 1982).

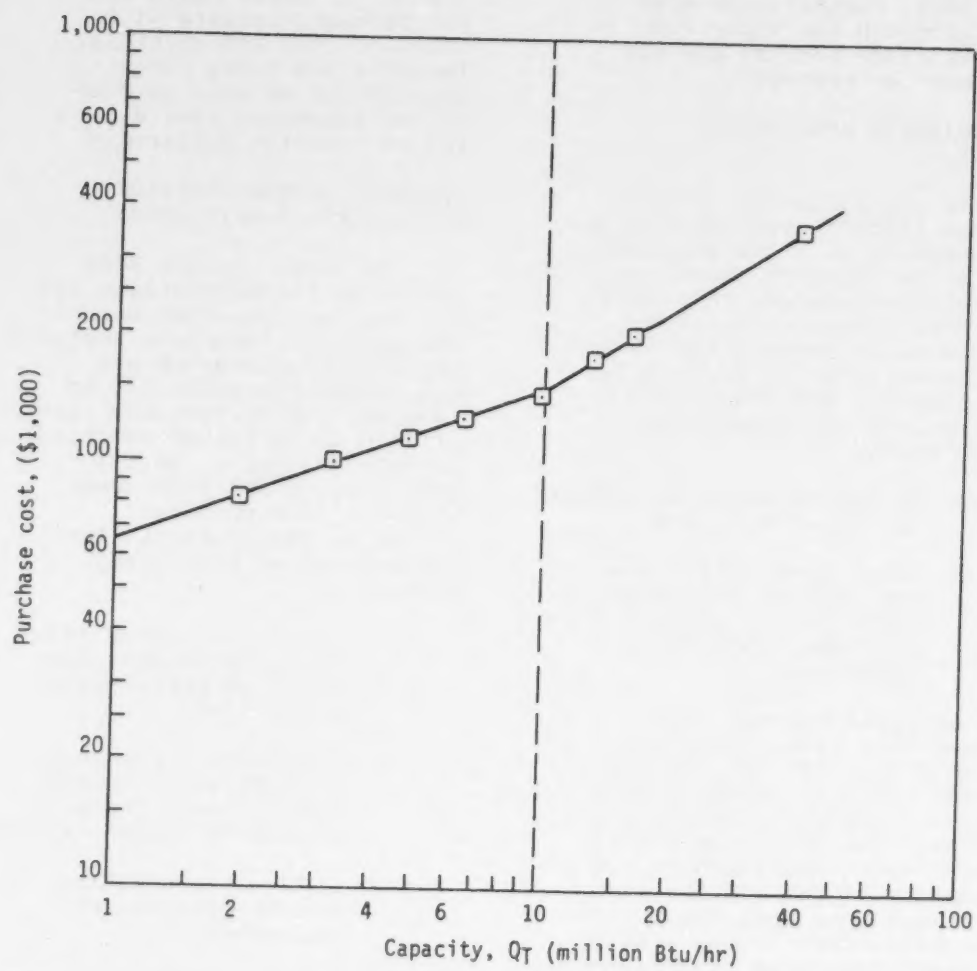


Figure 4. Purchase cost of multiple-chamber, hearth incinerators (July 1982).

For new systems, installation costs range from 25% to 100% of the purchased cost. A retrofit installation cost will approach the upper end of this range because the old unit must be removed.

QUENCH/WASTE HEAT BOILER ADDITION

If air pollution control devices (APCD's) such as venturi scrubbers or acid gas absorbers need to be added to existing incineration systems to comply with RCRA emission standards, some means of cooling the combustion gases prior to APCD entry must also be provided. Two alternatives are considered in the study:

- (1) Direct water-spray quenching to $<200^{\circ}\text{F}$, and
- (2) Waste heat boiler and post-boiler quench application to achieve the same temperature reduction.

Separate capital cost vs. gas flow rate curves are provided for high temperature quenches and for smaller, post-boiler quenches in Figures 5 and 6. Costs for high temperature quench towers are based on the assumption of $1800\text{--}2200^{\circ}\text{F}$ inlet gas temperature and, thus, interior refractory lining. Acid-resistant design is also assumed, although separate costs are presented for extremely severe service applications. Inlet gas temperatures of $400\text{--}600^{\circ}\text{F}$ and acid-resistant alloy construction are assumed for the smaller quenches. Installation costs are usually 30-40% of the purchased cost.

Equipment cost vs. gas flow rate curves are provided for waste heat boilers in Figure 7. These costs are for packaged boilers with standard trim and controls. Installation costs range from 30% to as much as 200% of the purchased cost depending on retrofit difficulty.

SCRUBBER SYSTEM ADDITION/REPLACEMENT/MODIFICATION

In order to meet RCRA standards for particulate and HCl removal, existing hazardous waste incineration facility retrofit requirements may range from virtually nil to complete particulate and acid gas scrubbing system addition. In terms of major capital additions or modifications, however, four retrofit scenarios were selected for the purpose of this study. These are:

- (1) Venturi scrubber addition/replacement for improved particulate collection,
- (2) Conversion from once-through water absorption of acid gases to a caustic recycle system,
- (3) Acid gas absorption column addition/replacement,
- (4) Total scrubbing system addition -- venturi scrubber and caustic recycle acid gas absorp-

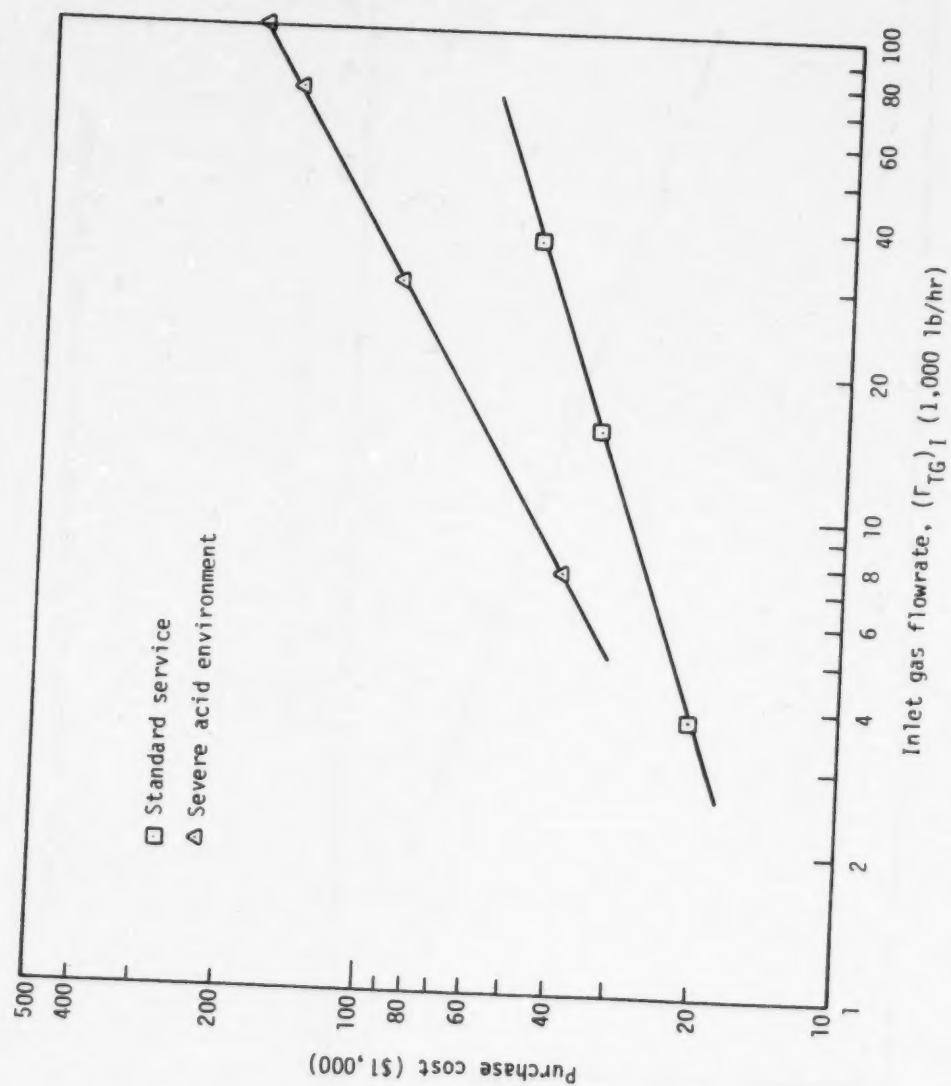


Figure 5. Purchase cost of quench towers (July 1982).

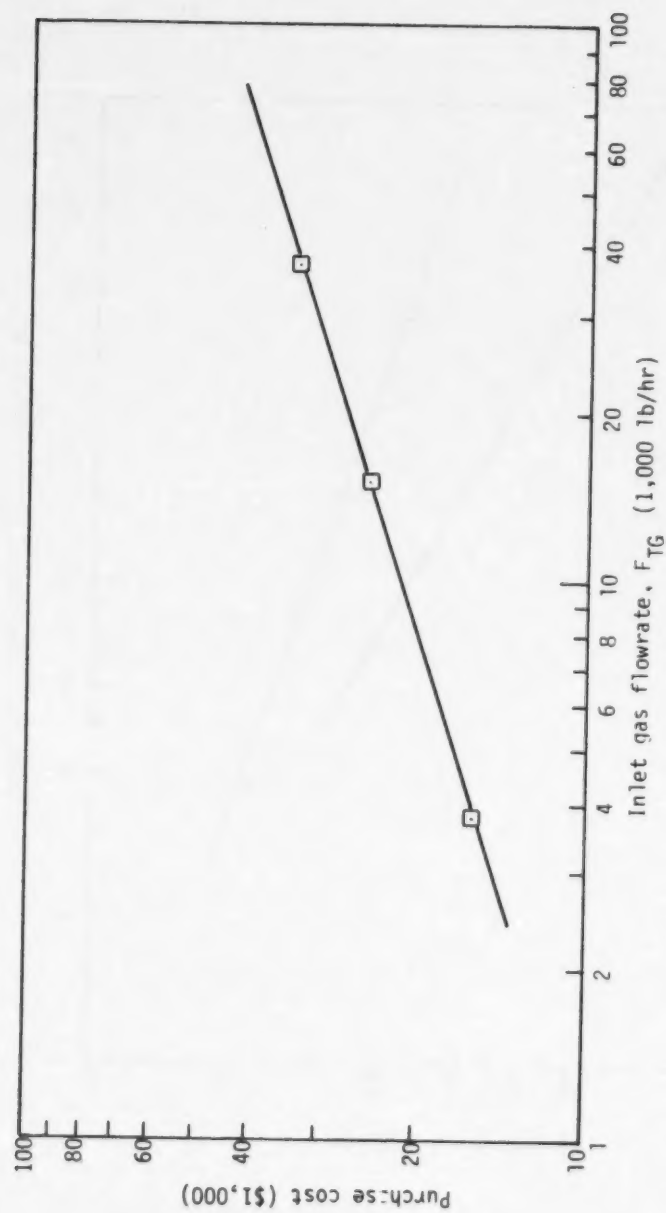


Figure 6. Purchase cost of low-temperature quenches (July 1982).

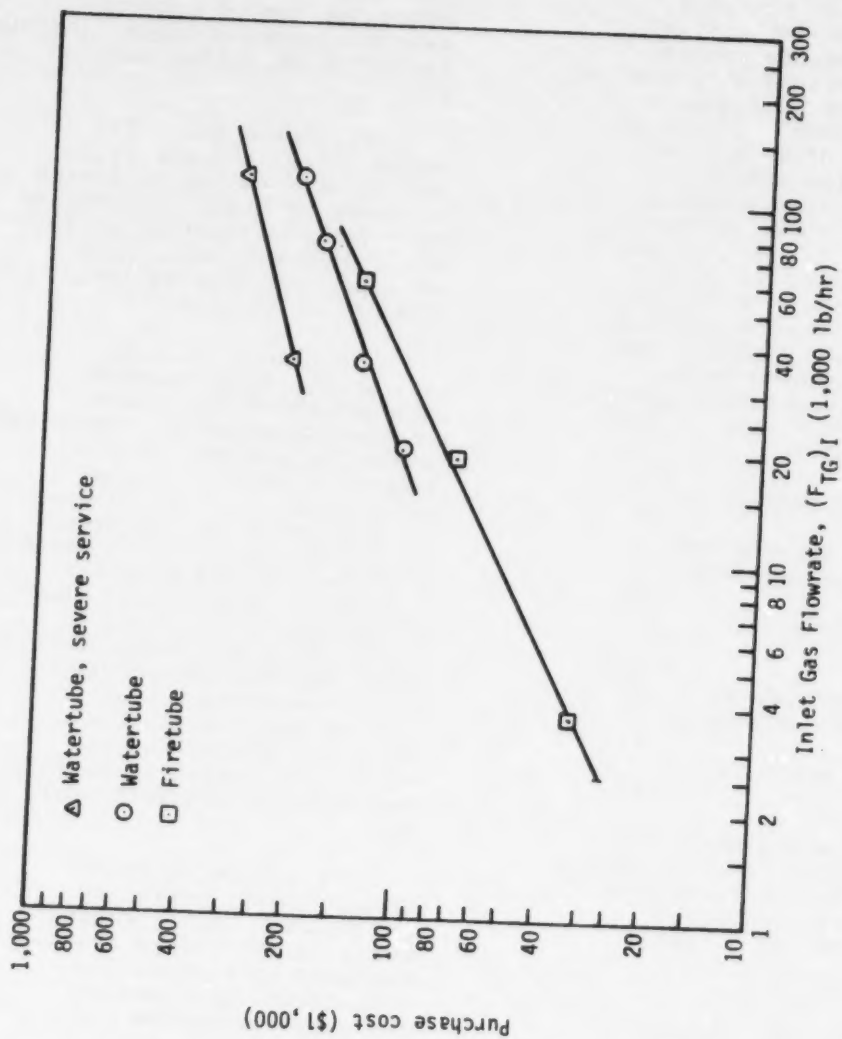


Figure 7. Purchase cost of waste heat boilers (July 1982).

tion system, plus fan and stack.

Purchased costs for complete scrubbing systems, including flue gas handling equipment, are presented in Figure 8. These costs are for typical 30"WC back pressure systems. For 100"WC pressure drop systems, the costs shown in Figure 8 can easily double. Conversely, the costs for 5" WC pressure drop systems (no venturi scrubber) are approximately 15% less than those presented in Figure 8. If no acid gas absorption system is needed, the cost reduction is approximately 40%. These guidelines, along with the component cost breakdown presented below, can be used to estimate equipment costs for virtually any retrofit scenario.

Venturi and wetted elbow	9%
Cyclonic separator and integral packed tower absorber	30%
Caustic system	17%
ID fan	18%
Stack	10%
Ductwork and piping	6%
Platform and foundations	4%
Instrumentation and controls	6%

Installation costs for scrubber system retrofit are quite site specific, however, 50-100% of the purchased equipment cost is a likely range.

FLUE GAS HANDLING SYSTEM MODIFICATIONS

In certain situations, particulate collection efficiency in the venturi

scrubber may be limited because the fan capacity is insufficient to handle the combustion gas flow at the pressure drop necessary for good venturi performance. If this is the case, then particulate emissions can be reduced (without reducing waste throughput) by simply replacing the fan.

Purchased costs for carbon steel and corrosion resistant fans are presented in Figure 9 and 10, respectively. Fan installation costs are relatively independent of capacity, usually running \$20,000 to \$30,000.

In Figure 11, cost vs. height relationships are presented for stacks of various diameter. Although stack replacement will not reduce emissions in itself, this retrofit scenario was considered at the request of the Office of Solid Waste for the purposes of their dispersion model-based risk assessment activities. Increased stack height reduces the maximum ground level concentration of emitted species, so the costs for adding taller stacks are needed to perform cost/benefit tradeoff analyses.

It should be noted that the costs presented in Figure 11 are purchased costs for FRP-lined stacks designed to receive low temperature gas exiting the scrubber system and fan. Erection costs are approximately equal to the fabricated material costs in all cases.

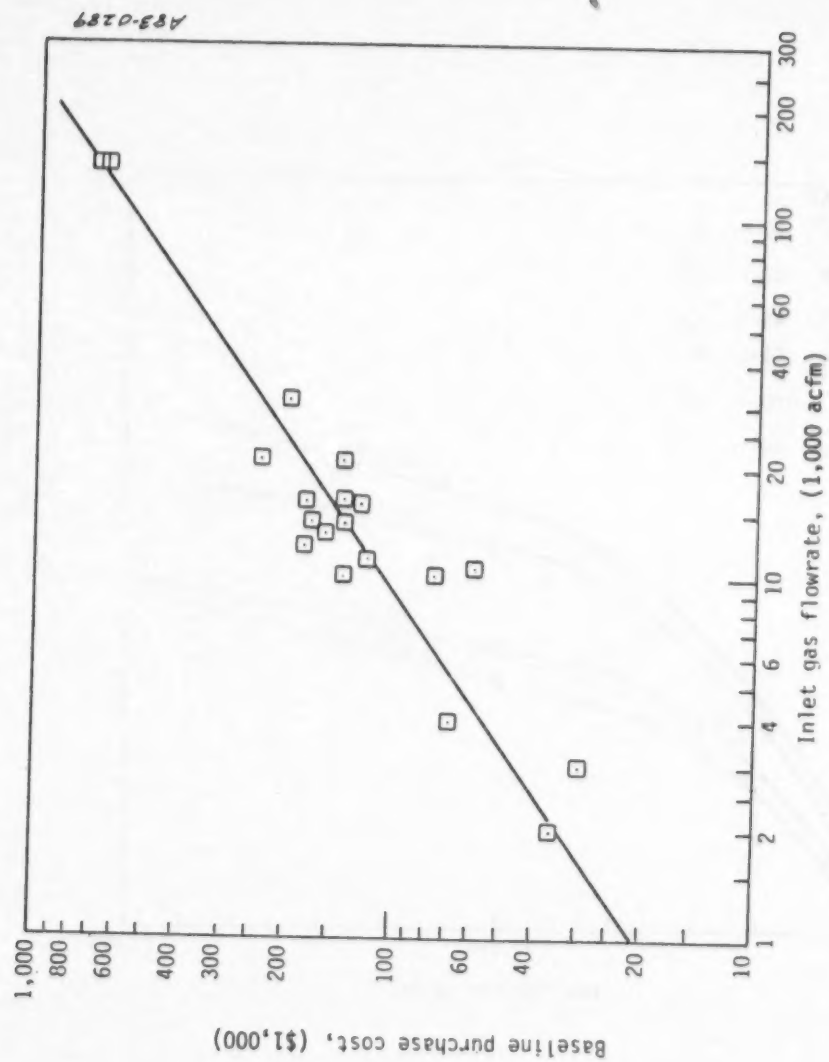


Figure 8. Purchase cost of scrubbing systems receiving 1,800° to 2,200°F gas (July 1982).

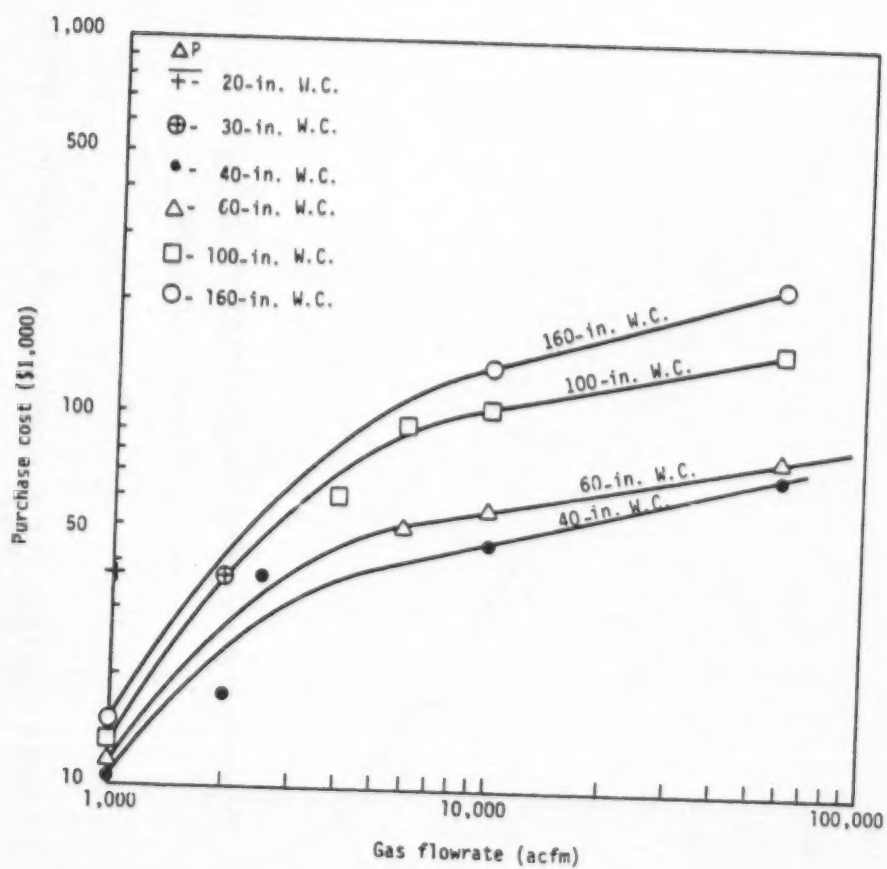


Figure 9. Purchase cost of carbon steel fans (July 1982).

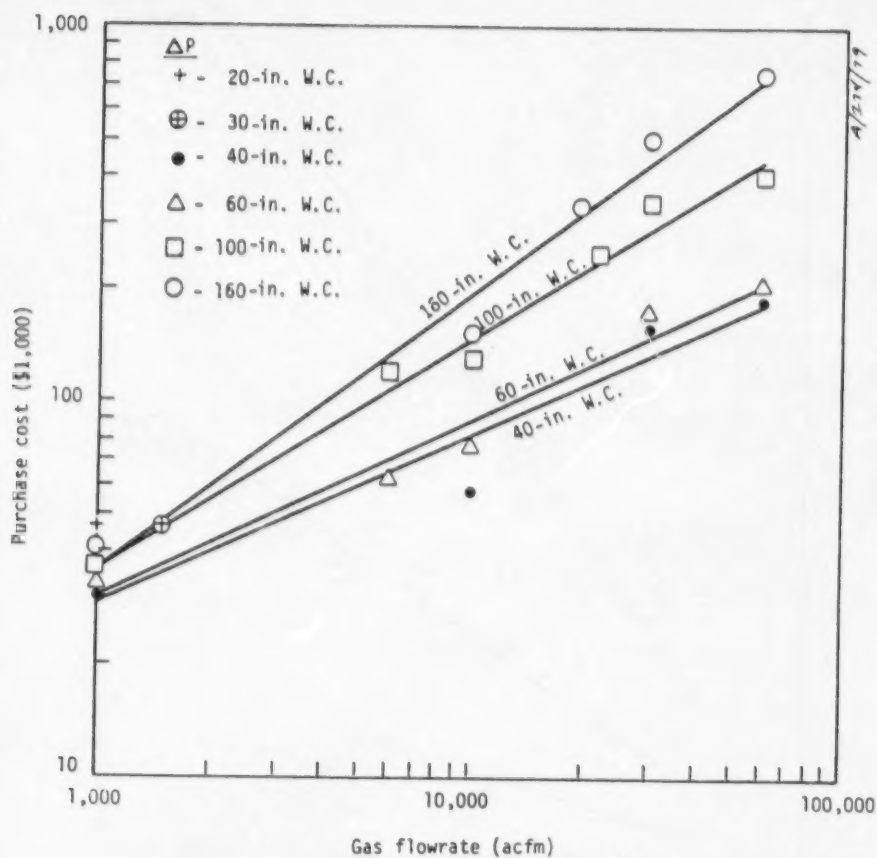


Figure 10 Purchase cost of corrosion-resistant fans (July 1982).

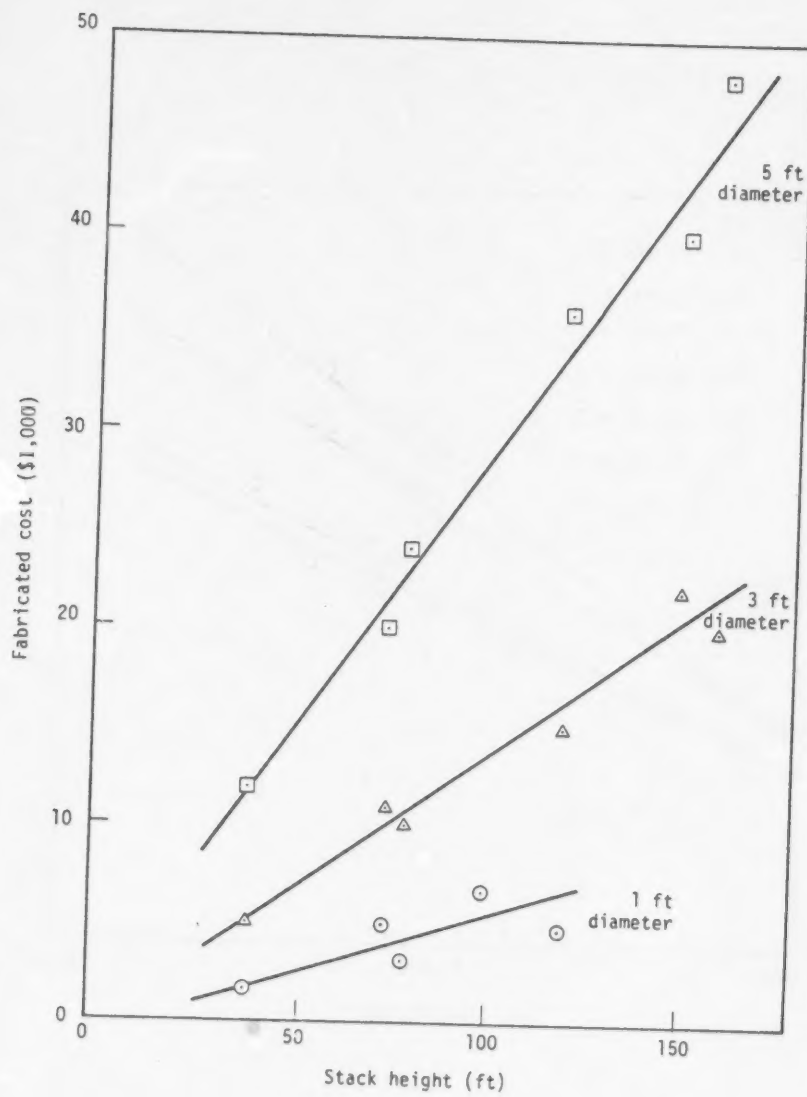


Figure 11 Fabricated cost of FRP stacks (July 1982).

INDIRECT COSTS

In addition to the direct costs for equipment and installation, the indirect costs associated with engineering, construction, and startup must be considered. For the purposes of this study, indirect costs are estimated as percentages of the total direct cost. These percentages are as follows:

Engineering	10%
Construction overhead	10%
Construction fee	8%
Startup	2%

Thus, the indirect costs are estimated to total approximately 30% of the direct cost for a given retrofit activity.

EXAMPLE

In order to illustrate how the information presented above can be used to estimate costs for major retrofit activities, the following example is provided.

Basis

A small multiple chamber hearth incinerator is being used to dispose of liquid process wastes and plant trash. The toxic components of the liquid waste are not difficult to destroy, so the unit is achieving 99.99% destruction efficiency. However, the system was installed prior to implementation of air emission standards, so no pollution controls are provided. Combustion gas is vented directly to a refractory-lined stack. As a result, the unit exceeds RCRA emission

standards for both particulate and HCl.

Retrofit Requirements

In order to achieve compliance, the existing stack must be bypassed and a complete scrubbing system -- venturi scrubber, HCl absorber, fan, and stack -- must be added. The mean particle diameter in the gas is approximately 2 μ m, so a 30" WC back pressure system is adequate. In addition, quenching can be accomplished in the venturi inlet. Space is available for the scrubbing system, so no special retrofit difficulties are encountered.

Costs

The combustion gas flow from the secondary chamber is 10,000 acfm at 1600°F. Therefore, from Figure 8 the purchased cost for the scrubbing system is approximately \$100,000. Installation runs about 50% of the equipment cost, so the total direct cost is \$150,000. Adding 30% for indirect costs, the total capital expenditure is \$195,000.

CONCLUSIONS

The study described in this paper is a basic, first cut effort to estimate potential costs for hazardous waste incineration facility retrofit. Because of the many site specific factors that impact retrofit costs, the accuracy of the estimates may be no better than - 50%

to 100% for some facilities. Large discrepancies between projected costs and actual costs are most likely in situations where space is limited, service relocations are required, interferences are encountered, or structural relocation is required. Where these problems are not encountered, the estimating methods described in this paper may achieve conceptual design accuracies of $\pm 30-40\%$

FULL SCALE DEMONSTRATION OF WET AIR OXIDATION
AS A HAZARDOUS WASTE TREATMENT TECHNOLOGY

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ABSTRACT

The purpose of this paper is to summarize the demonstration of Wet Oxidation of toxic and hazardous wastes at a full scale installation. This work is being done at Casmalia Resources, a commercial waste treater in California. The report will include data on continuous operating units of a commercial nature. It will also include testing on actual wastewaters produced by industrial clients in the Southwest portion of the United States.

I. INTRODUCTION AND SUMMARY

Wet Air Oxidation is a process which has been used to oxidize dissolved or suspended organic substances at elevated temperatures and pressures. The process is thermally self-sustaining with as low as 15 g/l COD organic feed concentrations and is therefore most useful for wastes which are too dilute to incinerate economically yet too toxic to treat biologically.

The process has been used to treat various wastes the last thirty to forty years. With the recent attention being focused on hazardous waste, much interest has been expressed in the use of Wet Oxidation as a means of destroying and/or detoxifying these hazardous wastes.

During the recent years much bench scale^{1,2} and pilot plant³ testing has been performed by various companies to demonstrate the applicability of Wet Oxidation on various hazardous organic wastes. Wet Oxidation units currently detoxify specific waste streams at several waste generation sites⁴.

The purpose of this project is to demonstrate Wet Oxidation of toxic and hazardous wastes at a full scale installation

which will be located at Casmalia Resources, a commercial waste treater in California. The project will enable development of data on continuous operating units of a commercial nature. It will also enable testing on actual wastewaters produced by industrial clients in the Southwest portion of the United States.

In the operation of the full scale wet oxidation unit, aqueous wastes selected from classified groups of organic wastes will be treated. These classified groups will be cyanide wastes, phenolic wastes, sulfide wastes, non-halogenated pesticides, solvent still bottoms, and general organic wastewaters. A selected waste containing compounds of a specific group will be run. Oxidation results will then be collated such that predictions might be made for all the compounds in a particular group.

Each waste to be tested will be selected from those collected by the commercial treater or those supplied by the Environmental Protection Agency or its supervising contractor. A preliminary autoclave Wet Oxidation test will be run where necessary to insure compatibility and treatability with the existing unit. It is expected that a continuous test of a minimum of eight hours will be run for each waste. The unit will operate at 2.3 m³/hr (10 gpm)

with a waste having a COD of up to 46 grams/liter. Waste with higher concentrations will be run at lower flow rates. The unit will be operated at its designed operating temperature of 280°C unless there is good cause to believe that the waste would be processed at a less severe condition. Samples of feed and effluent will be analyzed to determine effectiveness of treatment.

This paper will report on the status of the project.

II. Description of Wet Air Oxidation (WAO) Process

The Zimpro Wet Air Oxidation unit (See Figure 1), for this demonstration will process aqueous wastes at a designed reactor temperature of 280°C, a designed reactor pressure of 136 atm, a liquid waste flow rate of 2.3m³/hr (10 gpm). Waste will be mixed with compressed air and directed through the cold, heat-up side of the heat exchanger. The incoming waste-air mixture exits from the heat-up side of the heat exchanger and enters the reactor where exothermic reactions increase the temperature of the mixture to a desired value. The waste-air mixture exits the reactor and enters the hot, cool-down side of the heat exchanger and, after passage through the system pressure control valves, is directed to the separator. In the separator, the spent process vapors (non-condensable gases) are separated from the oxidized liquid phase and are directed into a two-stage water scrubber-carbon bed adsorber, vapor treatment system.

In the Wet Oxidation process, organic substances can be completely oxidized to yield highly oxygenated products and water. For example, organic carbon-hydrogen compounds can be oxidized to carbon dioxide and water, while reduced organic sulfur compounds (sulfides, mercaptans, etc.) and organic sulfides are oxidized to inorganic sulfate, usually present in the oxidized liquor as sulfuric acid. Inorganic cyanides and organic cyanides (nitriles) are oxidized to carbon dioxide, ammonia, or molecular nitrogen. It should be noted that oxides of nitrogen such as NO or NO₂ are not

formed in Wet Air Oxidation because the reaction temperatures are not sufficiently high to form them.

When incomplete oxidation of organic substances occurs, the reduced sulfur and cyanide are usually still oxidized to sulfate and carbon dioxide-ammonia provided a sufficient degree of oxidation is accomplished. However, incomplete oxidation or other organic compounds results in the formation of low molecular weight compounds such as acetaldehyde, acetone, and acetic acid. These low molecular weight compounds are volatile and are distributed between the process off-gas phase and the oxidized liquid phase. The concentration of these low molecular weight compounds (measured as total hydrocarbons (THC) expressed as methane) in the process off-gas is dependent on their concentration in the oxidized liquid phase, which is determined by, the degree of oxidation accomplished, the waste being oxidized, and the influent organic concentration of the waste.

III. Description of Commercial Test Site

The Wet Oxidation unit to be used in this demonstration work is located at Casmalia Resources Inc. secure chemical waste landfill in Santa Barbara County, CA. This landfill has been operating since 1972. The site is fully permitted as a hazardous waste treatment, storage and disposal facility pursuant to Section 25200 of the Health and Safety Code of the State of California Permit No. 42-001-78 has been amended to allow operation of the Wet Air Oxidation unit.

The Wet Air Oxidation unit has been purchased by Casmalia Resources and will be operated under contract by Zimpro Inc. It is anticipated that the unit will be used to treat those types or liquid wastes which will be banned from landfill on January 1, 1983 by order of the State of California.

Post-treatment of WAO effluent will be by evaporation ponds on the treatment site. After evaporation, any remaining residue (metals and salts) will be solidified and landfilled.

IV. Applications/Costs

Wet oxidation is best applied to dissolved or suspended organic or other oxidizable

WAO ELEMENTARY FLOW SHEET

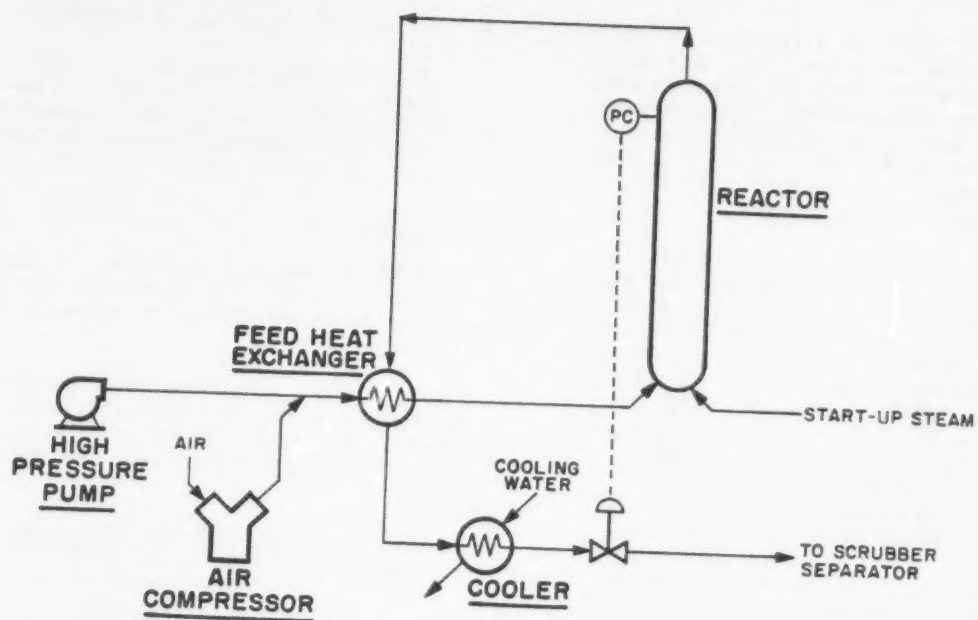


Figure I. WAO Elementary Flow Sheet

wastes. The process is thermally self-sustaining at relatively low concentrations (15,000 ppm COD). Since oxidation takes place in the liquid state, it is not necessary to evaporate the water. The process therefore is most useful for wastes which are too dilute to incinerate economically yet too toxic to treat biologically.

Figure II helps to illustrate the applicable waste concentrations. Wet oxidation operating costs are lower because of energy requirements. The difference between wet oxidation and conventional incineration for toxic waste treatment, for example, is significant and a function of oxygen demand.

With incineration, it is necessary to supply not only sensible heat and heat of vaporization of liquid, but also for heating vapors, combustion products, spent air and excess air up to a combustion temperature of between 800 and 1369°C. With wet oxidation, however, the only energy required is the difference in enthalpy between incoming and effluent streams. This value is typically 33,300 kcal/m³ for a waste low in organics, as opposed to 1.3×10^6 - 2.6×10^6 kcal/m³ for incineration. For a waste to become autogenous (thermally self-sustaining) in equipment of realistic size, a COD of approximately 15,000 ppm is required with wet oxidation; for thermal oxidation, approximately 400,000 ppm of COD are required.⁵

V. Wastes to be Treated

Unit Permits

The Wet Air Oxidation unit to be used for this demonstration has been permitted by the State of California Department of Health Services and the Santa Barbara County Air Pollution Control District to treat the following aqueous waste streams.

1. Cyanide wastes
2. Phenolic wastes
3. Sulfide wastes
4. Non-halogenated pesticides
5. Solvent still bottoms
6. General organic wastewaters

Wastes Specifically Exclude

1. The unit to be used for this test is not permitted to treat chlorinated aromatics such as hexachlorobenzene, chlorobenzene, dichlorobenzene or PCB's. Lab testing has already been completed.^{1,2} If it is desired to test these wastes on a full scale basis, it is possible to run these at Zimpro's facility in Rothschild, WI.
2. Acrylonitrile wastes are currently being treated at a minimum of five full scale installations. Therefore this wastewater will not be included as part of this work.

Waste Selection

Based on frequency of appearance on waste reports and quantities generated, the EPA has suggested the following compounds for this demonstration.

Zimpro intends to perform tests on waste-streams containing the following compounds. Six waste streams will be tested in a desired twenty-four hour run for each waste.

General Class	Specific Compounds
1. Methane	a. Chloroform b. Carbon tetrachloride c. Methylene chloride
2. Ethane	a. Vinyl chloride b. Dichloroethane c. 1,1,1-trichloroethane
3. Aromatics	a. Benzene b. Toluene c. Xylene
4. Others	a. Organic and inorganic cyanides b. Organic and inorganic sulfur compounds c. Phenols d. Pesticides (non-halogenated aromatics).

Zimpro is aware of available waste streams containing a mixture of several of the above compounds. We expect that demonstrations using these mixtures with analysis for the specific compounds listed in the above group will be completed.

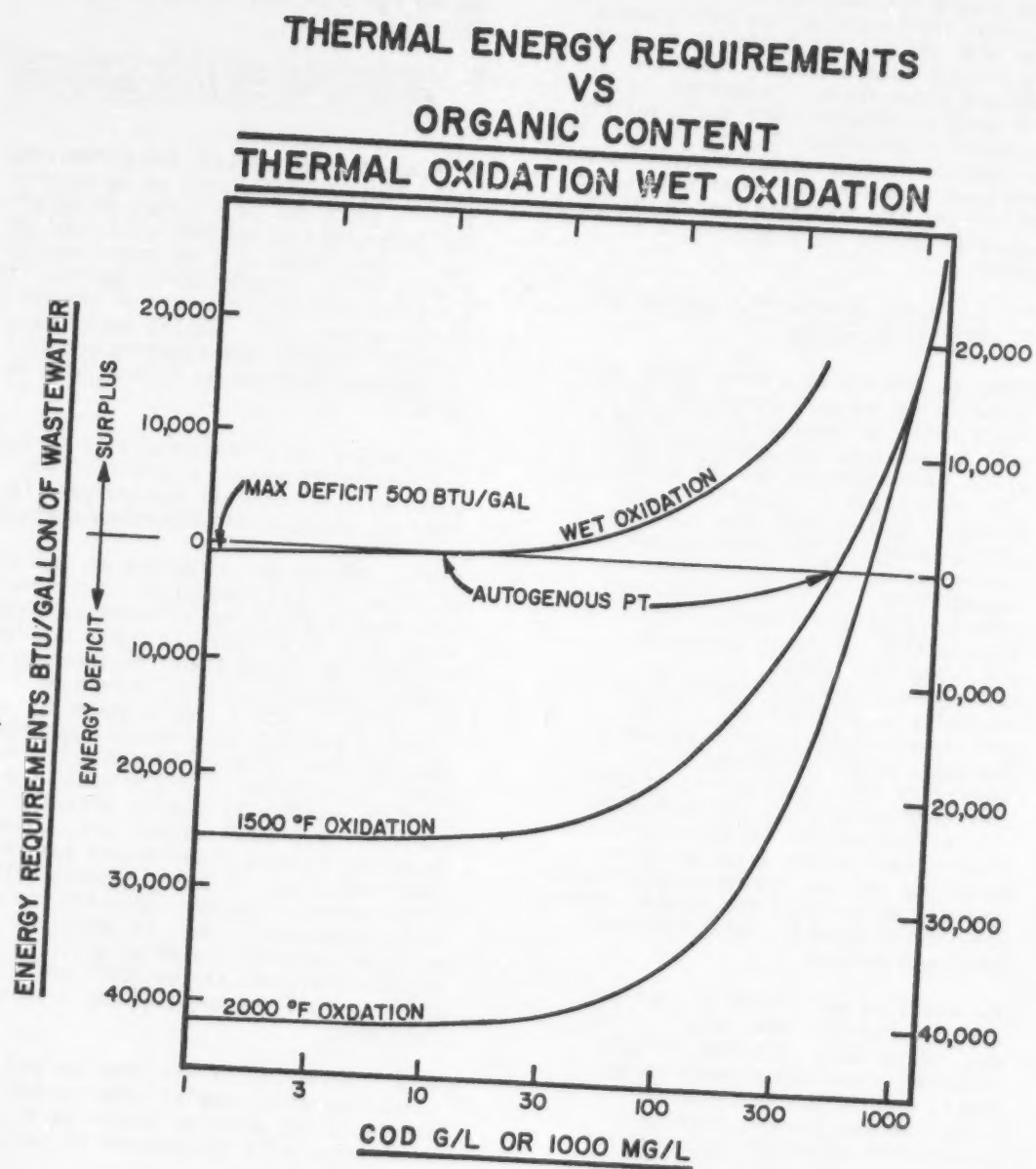


Figure II. Thermal Energy Requirements VS Organic Content

VI. Sampling and Testing Program

The program for sampling and testing the various liquid and gas streams associated with the Wet Air Oxidation process is divided into screening tests and demonstration tests. Screening tests are used to determine the applicability of Wet Air Oxidation in treating specific classes of wastes. Demonstration tests are used to determine the effectiveness of the Wet Air Oxidation unit while it is actually processing a specific class of waste.

A. Screening of Potential Wastes for Wet Air Oxidation

Prior to processing a given class of waste in the Wet Air Oxidation unit, representative samples of the waste will be obtained. A sample of this waste, approximately two (2) liters, will be shipped to Zimpro's laboratories. Upon receipt, the raw waste will be analyzed for chemical oxygen demand (COD), biological oxygen demand (BOD), pH, total solids, ash, soluble chloride, soluble fluoride and specific hazardous component, e.g., cyanide, phenol, sulfide, chlorinated aliphatic compounds, or non-halogenated pesticide. After preliminary analyses are completed, the waste will be oxidized in a laboratory shaking autoclave at the operating temperature and residence time of the Wet Air Oxidation unit. After oxidation the autoclave will be cooled and the non-condensable off-gas will be analyzed for oxygen, nitrogen, carbon dioxide, total hydrocarbons, and methane.

The oxidized waste will in turn be analyzed for COD, BOD, total solids, ash, pH, soluble chloride, soluble fluoride, dissolved organic carbon (DOC), and the specific component, e.g., cyanide, phenol, sulfide, chlorinated aliphatic compounds or non-halogenated pesticides. The percent destruction of the specific component will be calculated along with the autoclave oxygen demand.

Laboratory Wet Oxidation and analysis will also be used to determine materials of construction compatibility and the potential for scale formation in

the unit. Wastes which demonstrate high scaling potential or materials of construction incompatibility will be rejected for treatment in the Wet Air Oxidation unit.

B. Demonstration Period for Processing Wastes in the Wet Air Oxidation Process

A "demonstration period" for processing each selected waste will be conducted after a waste has been judged acceptable for processing in the Wet Air Oxidation unit. Each waste will be tested during a one (1) day "demonstration period," to determine the effectiveness of the Wet Air Oxidation unit. During each "demonstration period," the sampling and testing program outlined as follows will be used.

Upon arrival of a truckload of a screened and acceptable waste, a sample of the waste will be obtained and analyzed for COD, pH, and specific hazardous component.

During the Wet Air Oxidation of each class of waste, liquid composites of the influent raw waste and the effluent oxidized waste will be obtained. Liquid samples of these two streams will be taken on an hourly interval and the liquid samples will be made with 1 sample going for verification analysis at a second laboratory and the other going to Zimpro's laboratory for analyses. The raw waste and oxidized waste will each be analyzed for COD, BOD, pH, total solids, ash, soluble chloride, soluble fluoride and specific component, e.g., cyanide, phenol, sulfide, chlorinated aliphatic compounds, or non-halogenated pesticide. In addition, the oxidized waste will also be analyzed for dissolved organic carbon (DOC) and a GCMS scan will be made for any daughter compounds.

Grab samples of off-gas from the Wet Air Oxidation unit, sampled after carbon treatment but prior to discharge to the atmosphere, will be obtained in Tedlar gas sampling bags.

The sample of Wet Air Oxidation process off-gas will be analyzed for oxygen, nitrogen, carbon dioxide, carbon monoxide, total hydrocarbon, and methane. Gas sampling will be conducted when the Wet Air Oxidation unit is operating at

steady-state. Two replicate grab samples will be obtained each day that the waste is processed in the Wet Air Oxidation unit during the "demonstration period." One sample will be analyzed by Zimpro personnel and the other will be available for verification analysis by a second lab.

In addition to the above gas sampling program, the Wet Air Oxidation unit will be equipped with an on-line continuous total hydrocarbon analyzer for analysis of the process off-gas at a point before the carbon bed and also at a point before discharge to the atmosphere. The results of the continuous total hydrocarbon analysis will become part of the Wet Air Oxidation process operating record.

Analytical Procedures

The following analytical procedures, are used by Zimpro's laboratories.

1. Chemical Oxygen Demand
 - a. Macro method
 - b. Micro method
2. Dissolved Organic Carbon
3. Total Solids and Ash
4. Soluble Chloride
5. Soluble Fluoride
6. Cyanide
7. Phenols
8. Total Sulfides
9. Chlorinated Aliphatic Compounds
10. Non-Halogenated Pesticides
11. Gas Analysis
 - a. Oxygen
 - b. Nitrogen
 - c. Carbon dioxide
 - d. Carbon monoxide
 - e. Total hydrocarbons
 - f. Methane

VII. Status

The operating permits have been issued as of October 1, 1982. It is expected that installation to be completed by late November and that waste processing will begin late 1982.

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ENGINEERING GENES IN YEAST FOR BIODEGRADATIONS

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ABSTRACT

In order to obtain a yeast gene sequence which would allow the isolation of different P-450 genes for use in specific biodegradations, we have constructed a *Candida tropicalis* 750 genomic library. This genomic library contains *C. tropicalis* gene sequences stored as 5 to 10 kilobase pair lengths of DNA inserted into the shuttle vector pAB107. The library contains DNA sequences which will complement mutations in a *Saccharomyces cerevisiae* strain deficient in the biosynthesis of both histidine and adenine; thus at least those *C. tropicalis* genes can be functionally expressed in *S. cerevisiae*. One *C. tropicalis* cytochrome P-450 sequence codes for an enzyme which catalyzes the α -hydroxylation of n-alkanes. This hydroxylation is the first step in a catabolic pathway which allows the organism to grow on tetradecane as sole carbon and energy source. Mutants of a closely related yeast exist which are blocked in different steps of n-alkane utilization, including some which may be deficient in this hydroxylase. Consequently, we plan to screen the library for this gene by transforming these mutants with the library DNA and looking for clones which have acquired the ability to use tetradecane as a carbon and energy source. In separate experiments we have indicated that *S. cerevisiae* D7 is heterozygous for the amount of P-450 since haploid cultures form 2:2 segregation ratios of high and low levels of P-450.

INTRODUCTION

A group of chemicals which cause concern as risks to human health are the so-called recalcitrant compounds (1). These compounds are usually hydrophobic and are resistant to physical or biological decomposition in the environment. Because of their chemical stability they are available for eventual redistribution in ways which bring them into contact with man. This can happen through contamination of drinking water sources or through bioaccumulation in the food chain. By either route, the hydrophobic nature of many of these xenobiotic compounds leads to their incorporation into the fatty tissue of the body.

If these recalcitrant compounds were

entirely inert, and thus refractory to mammalian metabolic conversion, they might present relatively minor problems. However, many act as signals to alter gene expression and cause profound changes in the type and quantity of metabolic enzymes in the cells of many organs and tissues. The major group of "induced" enzymes are complex oxidative enzymes known as the cytochrome P-450 monooxygenases. These enzymes, present in the tissues either at background levels or at elevated levels following induction, can result in the metabolism of recalcitrant compounds to cytotoxins, direct acting mutagens, carcinogens, or teratogens. However, the different enzymes which are induced in this manner include activities which detoxicate xenobiotic chemicals as well as those which increase the

toxic effects of such compounds. In such cases it can be stated that the enzymes necessary for metabolism of environmentally recalcitrant compounds do exist, but in the wrong places.

By combining recent advances in gene engineering, microbiology and biochemistry, it should be possible to develop microorganisms which could detoxicate a recalcitrant compound in the environment before it came in contact with man. Any organism possessing the desired activity could be used as a source of monooxygenase genes to be manipulated. For the compounds where biotransformation is understood, the best source could be the genes of those organisms. Environmental biodegradations are primarily effected by mixtures of bacteria, yeasts, molds and other fungi. Of these, certain species of bacteria and yeasts grow rapidly as single cells and are well characterized both with respect to genetics and to the relevant recombinant DNA techniques, and so are best suited for genetic manipulation. Both possess monooxygenase systems which include cytochrome P-450 hemoproteins. However, the systems found in yeasts are quite similar to those found in hepatic tissues and in other eucaryotic cells, whereas those in bacteria are considerably different (18).

Based upon these relationships we have initiated the genetic engineering of cytochrome P-450 expression in yeast for the degradation of hazardous organic wastes. Our first experiments are intended to obtain a probe for cloned P-450 sequences and to gain a practical understanding of the P-450 systems which operate normally in the yeast *S. cerevisiae*. In this paper we report on progress made toward these objectives.

MATERIALS AND METHODS

Strains

The *Saccharomyces cerevisiae* haploid strain BWG 2-9A (MATa adel-100 his4-419 ura3-52) was a gift from L. Guarente. A recA⁺ variant of *E. coli* JW355 (F⁻ araDI39 (ara, leu) 7697, lacX74 galK galU recA rpsL hsdR) was a gift from J. Williams. *C. tropicalis* 750 was obtained from the American Type Culture Collection, Rockville, MD. Haploids of *S. cerevisiae* D7 were generated from diploid stocks provided by E. Nestmann and by F. Eckardt.

Enzymes

Restriction enzymes were from New England BioLabs. T4 DNA ligase and bacterial alkaline phosphatase were from Bethesda Research Laboratories. Enzymes were used as recommended by the suppliers.

Preparation of DNA

High molecular weight yeast DNA was prepared by the method of Cryer et al. (6). Covalently closed circular plasmid DNA was isolated from *E. coli* using the method of Holmes and Quigley (10). In some cases this plasmid DNA was purified by CsCl/ethidium bromide banding (5). Plasmid DNA from yeast was isolated using the method of Nasmyth and Reed (15). Partial digestions with the restriction enzyme *Sau3A* I were performed as described (12) to ensure maximum sequence representation of restriction fragments in the 5 to 10 kilobase pair (kbp) length range.

Transformation Procedures

Yeast transformations were performed using the procedure of Beggs (3) as modified by Sherman et al. (19). Bacterial transformations were performed using a method devised by J. Williams (personal communication). One ml of an overnight culture of the *E. coli* in L broth (10 g/l Bacto-tryptone, 5g/l Bacto-yeast extract, 5 g/l NaCl) is used to inoculate 50 ml of L broth. The culture is incubated at 37°C with shaking until the absorbance at 650 nm reaches 0.2. The culture is then chilled on ice for 10 min, collected by centrifugation (5 min, 3000 x g), resuspended in 4 ml sterile cold 0.1 M CaCl₂, and stored 25 min on wet ice. The cells are then collected by centrifugation (5 min, 3000 x g) and resuspended very gently (2 to 4 hr on rotating platform in a cold room) in 0.4 ml cold 0.1M CaCl₂. A cold pipet is used to add an aliquot of the cell suspension (0.1 ml) to 0.02 ml of the DNA which is dissolved in 10mM Tris-Cl, 0.1mM EDTA; pH 8.0. The mixture is incubated for 15 min at 0°C, 2 min at 45°C, and then placed at 37°C. Immediately, 1.0 ml of pre-warmed 37°C L broth is added and the mixture incubated with gentle shaking for 1 hr. Aliquots (0.1 ml) are then plated on L agar plates supplemented with ampicillin (25 µg/ml) and incubated overnight at 37°C.

Gel Electrophoresis

Gel electrophoresis of DNA was performed as described by Mickel et al. (13).

The isolation of DNA fragments from low melting agarose gels followed the procedure of Langridge et al. (11).

Vector

The shuttle plasmid pABI07 was obtained from L. Melnick. It contains pBR322 sequences which express tetracycline and ampicillin resistance markers and allow replication in *E. coli*. Also present is the *S. cerevisiae* URA3 gene for use as a selectable marker, plus an ARS1 sequence (21) which allows the vector to replicate in yeast.

Media

Yeast were ordinarily grown either on a complex medium for routine growth (YPDG) or a synthetic medium (SD) with the appropriate supplements (19).

Cytochrome Determinations

C. tropicalis was grown in YEPD medium containing 20% glucose (22) and also in medium containing 0.5% tetradecane (8). Haploids of *S. cerevisiae* were grown in YEPD medium containing 20% glucose. Cells were collected by adding an equal volume of ice-cold phosphate buffered saline (PBS) to cultures in the midlog growth phase. After centrifugation (5 min, 4000 x g), the cell pellet was washed once with PBS and resuspended in 0.1M potassium phosphate buffer (pH 7.4) at a concentration of 0.1 g wet weight of cells/ml. The cytochrome P-450 and cytochrome P-420 contents of whole cell suspensions were determined with a Perkin-Elmer model 575 spectrophotometer using the method of Omura and Sato (17). Cytochrome contents (nmole/g wet weight of whole cells) were calculated using molar extinction coefficients of $91 \text{ cm}^{-1} \text{ mM}^{-1}$ (17) and $110 \text{ cm}^{-1} \text{ mM}^{-1}$ (20) for cytochrome P-450 and cytochrome P-420, respectively; corrections to the cytochrome P-420 values due to the absorption of cytochromes P-450 at 420nm were taken according to the procedure of Guengerich (9).

RESULTS

Our initial experiments have been directed towards two goals. The first is to obtain any yeast P-450 gene sequence which may then be used as a probe to isolate other P-450 genes, as was done by Hall and colleagues for the yeast iso-cytochrome C genes (14). The second goal is to begin to understand the mechanism(s) by which the

level of P-450 gene expression in *S. cerevisiae* is modulated so that the expression of recombinant genes may be controlled.

One approach to obtaining the initial P-450 gene was to construct a genomic library of *Candida tropicalis* 750. This single celled yeast and a closely related organism *Saccharomyces lipolytica* can grow on tetradecane as sole carbon and energy source. The initial step in this catabolic pathway is catalyzed by a highly inducible cytochrome P-450 enzyme, n-alkane hydroxylase. We have confirmed that the cytochrome P-450 content in *C. tropicalis* 750 increases when tetradecane rather than glucose is used as a carbon source (Fig. 1). *S. cerevisiae* does not express this pathway and can not grow on n-alkanes. We chose initially to prepare a genomic library for *C. tropicalis* and to test the transfer of genetic information from this library to *S. cerevisiae*.

Construction of the *C. tropicalis* 750 library

The library was made by inserting random restriction fragments of *C. tropicalis* 750 DNA into the plasmid pABI07 (see Fig. 2). The resultant recombinant plasmid mixture was used to transform *E. coli* to yield a large number of different *E. coli* clones, each containing a recombinant plasmid with an inserted fragment of *C. tropicalis* DNA. The number of different clones needed to assure a greater than 99% chance of having a given segment of the *C. tropicalis* genome is less than 12,800 (4).

High molecular weight DNA of *C. tropicalis* (100 kbp) was partially digested with the restriction enzyme *Sau3A* I so that the number average molecular weight of the digested DNA peaked in the region corresponding to 5 to 10

kbp fragments. This DNA was then separated by electrophoresis on a 0.8% low-melting agarose flat bed gel. The region of the gel corresponding to restriction fragments of 5 to 10 kbp was excised and the DNA isolated.

DNA of the vector pABI07, after complete digestion with *Bam*H I and treatment with bacterial alkaline phosphatase, was isolated in the same manner as the *C. tropicalis* DNA.

The two DNAs were then ligated for 24 hr at 14.5°C in a 0.5 ml reaction mixture containing 40 µg pABI07 DNA, 5 µg *C. tropicalis* DNA, and 2.5 units of T4 DNA ligase in

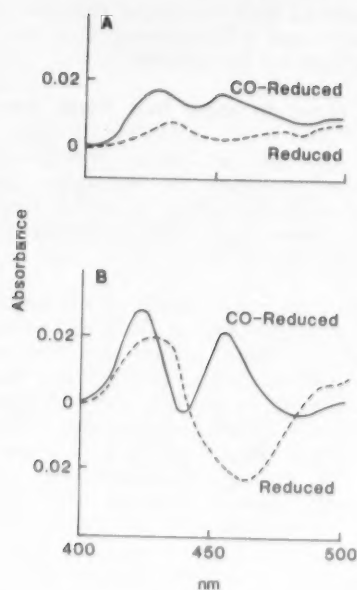


Figure 1. Absorption spectra of *C. tropicalis* 750. Cells in log phase of growth were resuspended at 0.1g wet weight whole cells/ml, dithionite-reduced vs. dithionite-reduced plus CO. A: grown on 20% glucose; B: grown on 0.5% tetradecane.

the buffer recommended by the supplier. Because the pAB107 DNA had been treated with alkaline phosphatase, it could not self-ligate and generate transformants which contain no *C. tropicalis* DNA sequences.

Approximately 1/3 of this ligation mixture was used to transform *E. coli* which was then plated to yield 29,000 colonies on L-agar plates supplemented with 25 µg/ml ampicillin. The colonies were rinsed from the transformation plates with L broth and collected by centrifugation. Part of this cell population was resuspended at 1.4×10^{11} cells/ml in L broth containing 8% dimethyl sulfoxide and stored at -80°C. The remainder was used to isolate plasmid DNA, which was purified by banding in CsCl, and then stored at 5°C in 10

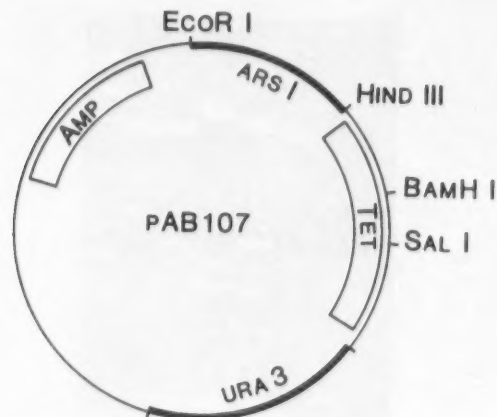


Figure 2. The circular shuttle plasmid pAB107, (obtained from L. Melnick, Univ. of Rochester). The heavy lines correspond to the locations of yeast sequences which allow autonomous replication in *S. cerevisiae* (ARS I) and complementation of a *ura3* mutation in yeast genomic DNA (URA3). The lighter portions of the circle correspond to pBR322 DNA sequences and contain a DNA replication origin which allows the plasmid to replicate in *E. coli*. The closed boxes mark the locations of regions in the plasmid which code for resistance to ampicillin (Amp) and tetracycline (Tet). Foreign DNA sequences inserted at the BamHI site inactivate the tetracycline resistance gene. Consequently, the phenotype of plasmids containing inserted DNA sequences at the BamHI site is Amp^r-Tet^s. The plasmid is 6.3 kbp in length.

mM Tris-Cl, 0.1 mM EDTA at pH 8.

Four random clones from the library were grown in liquid culture. Their plasmids were extracted, cleaved with EcoR I, and the DNA fragments were separated by electrophoresis on a 0.8% agarose gel. All 4 contained inserted DNA sequences (Fig. 3). Based on examination of an additional 20 clones, approximately 70% of the clones contain inserted DNA sequences.

Isolation of Clones Which Complement the *adel* and *his4* Mutations

S. cerevisiae BWG 2-9A is auxotrophic for histidine, uracil, and adenine because of mutations in its *ura3*, *his4*, and *adel* genes. We transformed this yeast strain with the library

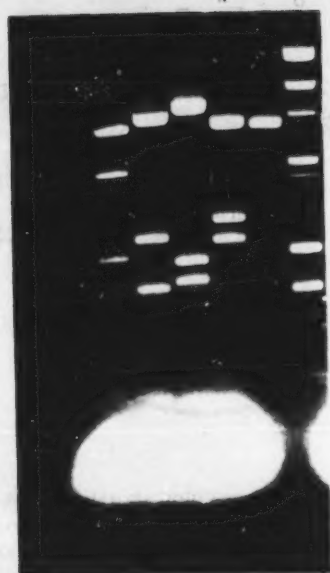


Figure 3. EcoR I digests of random clones from the *C. tropicalis* library. Lanes 1-4 are plasmid preparations of 4 randomly selected clones digested with EcoR I. Lane 5 is pABI07 cut with BamH I. Lane 6 is a mixture of DNA digests: charm 4A (digested with BamH I); pBR322 (digested with EcoR I and Rsa I). The eight strongest bands from top to bottom are 4.9, 23.3, 10.4, 7.0, 4.4, 3.9, 2.1 and 1.6 kbp. The region of intense fluorescence at the bottom of the gel results from RNA which is not removed from the plasmid preparations unless they are banded in CsCl/ethidium bromide.

DNA and selected for yeast colonies which grew in a minimal medium unsupplemented with uracil. Only those colonies (approximately 27,000 from 3.4 μ g total library DNA) which had received a functional *URA3* gene from the vector pABI07 were able to grow. It should be emphasized that the vector itself contains the functional *URA3* gene and that this initial transformation simply selects for the vector pABI07 and not for a specific *C. tropicalis* insert. We then added 30 ml of sterile water to the top agar containing the yeast transformants from the transformation plate, and ground in a Waring blender. This material was washed by 3 centrifugations and resuspensions in sterile water.

In order to select clones containing the *C. tropicalis* DNA sequences which would complement the *his4* and *adel* mutations in *S. cerevisiae*, aliquots of the washed material were then plated on minimal plates lacking either adenine or L-histidine. We obtained 30 yeast colonies that no longer required adenine for growth and 875 colonies that no longer required histidine for growth.

In order to show that these transformants had lost their auxotrophic requirements because they had received a recombinant plasmid which provided the necessary gene sequences, we recycled the plasmids through *E. coli* and then back into untransformed *S. cerevisiae* BWG 2-9A.

Ten clones from each of the adenine and histidine transformant collections were grown separately in liquid culture and their plasmid DNAs extracted. The DNAs from the yeast adenine transformants and the histidine transformants were pooled separately. These two pools of DNA were then used to transform *E. coli*. The *E. coli* transformants were not plated but allowed to grow overnight in L broth supplemented with 25 μ g/ml ampicillin. The plasmid DNA from each *E. coli* culture was then extracted and used to transform *S. cerevisiae* BWG 2-9A. Plasmid DNA originating from the yeast adenine transformants gave rise to adenine transformants in yeast after passage through *E. coli*. The plasmid DNA originating from the yeast histidine transformants also behaved in the expected way.

The *E. coli* plasmid preparations used in the secondary yeast transformations described immediately above were also analyzed by electrophoresis on a 0.8% agarose gel after restriction with EcoR I, see Fig. 4. These plasmid preparations originating from either the yeast adenine transformants (lane 3) or the histidine transformants (lane 4) appear to contain more than one type of plasmid. This could arise from including variable portions of the yeast genome flanking the *adel* and *his4* genes.

Prospects for Detection of Clones Which Code for Expression of n-alkane Hydroxylase.

Based upon these results, this gene library should include clones containing inserted DNA sequences for each of the several genes involved in the n-alkane oxidative pathway, including the gene for the cytochrome P-450 enzyme n-alkane hydroxylase. The most direct approach to

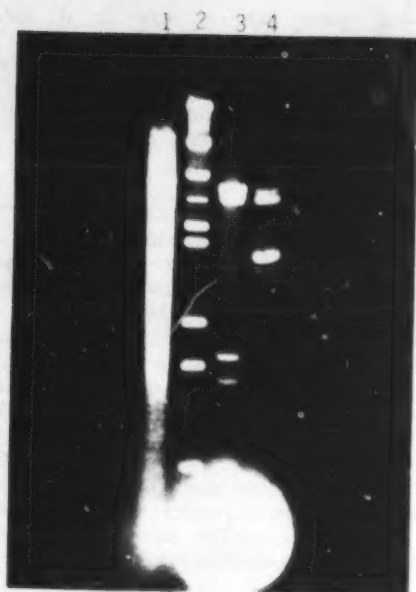


Figure 4. EcoR I digests of recombinant plasmids which complement the *his4* or *adel* mutations in yeast. Lane 1 is an EcoR I digest of total library DNA in pAB107. Lane 2 contains DNA size markers as in Fig. 3. Two smaller bands (680 and 506 bp) can be seen in this run. Lanes 3 and 4 contain EcoR I digests of plasmids which complement the *his4* (lane 3) or *adel* mutations in *S. cerevisiae*.

obtaining this P-450 gene is to transform a recipient yeast strain lacking the function with the library of cloned sequences. Recipient yeast cells that gained the P-450 gene could be easily recognized if the gene conferred the capacity for growth on tetradecane. However several genes are involved in the n-alkane utilization pathway, and it is not known how many of these are missing in *S. cerevisiae*. We have conducted two experiments in which more than forty thousand cells of strain BWG2-9A received library clones, as indicated by expression of *URA3* on the cloning vector, but none of these recipients grew on tetradecane. Fortunately mutants in another yeast exist which are blocked in different steps of n-alkane utilization. These are the *alk* mutants of *Saccharomycopsis lipolytica* (2), a sporulating variant of a *Candida* species similar to *C. tropicalis* (16). The phenotype of some of these mutants suggests that they may be specifically deficient in the P-450

hydroxylation reaction. In collaboration with Dr. J. Bassel we plan to screen our gene library by transforming this sub-set of *alk* mutants with the library DNA and looking for clones which have acquired the ability to utilize tetradecanes.

Cytochrome P-450 Levels in *S. cerevisiae*

We have begun an examination of P-450 inducibility in *S. cerevisiae* since strains which are differentially inducible for P-450 will be useful as recipients in future gene engineering experiments. Diploids of *S. cerevisiae* D7 were sporulated, and asci were dissected using a micromanipulator. Haploid cells from each ascospore were grown to log phase in YEPD medium containing 20% glucose, conditions which had been previously shown to increase the levels of P-450 in *S. cerevisiae* (22). Whole cell suspensions of haploid segregants were used for spectral determinations of both cytochrome P-450 and cytochrome P-420, an inactive form of P-450. The results of these measurements, shown in Table I, indicate that *S. cerevisiae* D7 is heterozygous for levels of P-450, with ascospores generally segregating 2:2 (high P-450:low P-450). Interpretation of these ratios is complicated by the 2:2 segregations of high P-420:low P-420, in that the levels of P-420 were not always in reverse relationship to the levels of P-450.

DISCUSSION

We are using a gene engineering approach to achieve the biodegradation of a broad range of recalcitrant compounds of environmental concern. The focus is on compounds which cause their adverse effects after they are taken up by cells and become metabolized to more reactive forms — such metabolites eventually effect cell damage or are detoxicated by the cell. The rationale is to modify yeasts to do this metabolic activation-detoxication. This genetic capacity would then be used in these yeasts; or would be transferred for use in related microorganisms occurring in the environment close to the origin or location of the problem compound.

We have shown that genes from one genus of yeast can be transferred into and expressed in another genus of yeast in the case of *C. tropicalis* and *S. cerevisiae*. Dickson (7) has shown that the *Kluyveromyces lactis* β -galactosidase gene can be transferred into and expressed in *S. cerevisiae*. It appears that the signals necessary for the transcription and translation of genetic

TABLE 1. CYTOCHROME P-450 AND P-420
CONTENT OF *S. CEREVISIAE*
STRAIN D7 HAPLOIDS

Haploid segregants ^E	Cytochrome P-450 nmoles/g ⁺	Cytochrome P-420 nmoles/g
3a	0.80	0.30
3b	0.46	0.17
3c	0.34	2.66
3d	0.69	2.34
5a	0.34	2.02
5b	0.91	.34
5c	0.23	2.83
5d	0.57	0.21
7a	1.32	0.49
7b	0.44	1.98
7c	0.36	1.32
7d	0.99	0.64

^EHaploids from three asci of *S. cerevisiae* were grown in YEPD medium containing 20% glucose.

⁺nmoles/g wet weight of whole cells.

information are similar enough between the two genera to allow the isolation of a cloned P-450 gene from *C. tropicalis* followed by analysis of its expression in *S. cerevisiae*. This cloned gene may then be used as a hybridization probe to isolate other P-450 genes that code for enzymes involved in the biodegradation of recalcitrant compounds.

The level of cytochrome P-450 expression from the newly introduced gene must be compatible with the levels of the other components of the P-450 system such as NADPH and NADPH cytochrome P-450 reductase. Expression of a cloned P-450 gene in yeast could be controlled by using appropriate promoter sequences and other DNA signals for expression. This expression can also be influenced by introducing the gene on a plasmid which replicates at a high copy number in yeast, or on a plasmid such as YCpl9 which is fairly stably maintained at about one copy per nucleus, or by integrating

the P-450 gene into a site in a normal chromosome or chromosome pair. The segregation of high and low levels of P-450 which we have observed in haploids of *S. cerevisiae* may also be a useful tool in controlling the expression of P-450 in our genetically engineered yeast.

Our goal is the production of a set of yeasts each of which is capable of a safe, high-level biooxidation of a different hazardous compound or compounds. These yeast strains alone or together could be tested for the bioconversion of hazardous byproducts in industrial processes and for the elimination of such problems in spills or dumps. Since different species of yeast or fungi are likely to better tolerate the ecological conditions presented by various noxious environments, these strains could be used for secondary gene engineering among naturally occurring eucaryotic microorganisms, in order to establish the preferred detoxicating variants.

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